U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-252 243

EVALUATION OF THE CONTROLLABILITY OF SO2 EMISSIONS FROM COPPER SMELTERS IN THE STATE OF ARIZONA

PACIFIC ENVIRONMENTAL SERVICES,
INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

JUNE 1975

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA909/9-76-003	2.	3. Recipient's Accession No.
4. Title and Subtitle: Evaluation of the controllability of SO_2 emissions from copper smelters in the state of Arizona			5. Report Date: June 1975 6.
7. Author(s): I.J. Weisenberger, G.E. Umlauf			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: Pacific Environmental Services, Inc 1930 14th St. Santa Monica CA 09404			10. Project/Task/Work Unit No. 11. Contract/Grant No. 68-02-1354
12. Sponsoring Organization Name and Address: U.S. Environmental Protection Agency Region IX 100 California St., San Francisco CA 94111			13. Type of Report & Period Covered: final 14.

15. Supplementary Notes

16. Abstracts

The objective of this study was to conduct smelter inspections and engineering analyses of existing, planned, available or potentially available SO2 control systems in support of preparation of regulations for copper smelters in the Arizona portion of Region IX. The inspections and analyses were to assess the 1) feasibility of upgrading existing or planned permanent controls, 2) feasibility of operational changes to improve control, and 3) applicability of available or potentially a ailable constant emission control technology.

A total of seven copper smelters in the State of Arizona were reviewed. The major source of uncontrolled SO2 emissions at the present time in the average smelter is the reverberatory furnace since most smelters control converter offgases. Alternate control techniques are discussed in general.

17. Key Words and Document Analysis. 17a. Descriptors

Sulfur dioxide
Air pollution control
copper
Arizona
Industrial wastes

17b. Identifiers/Open-Ended Terms

copper smelters
smelters
Reverberetory furnace

17c. COSATI Field Group

18. Availability Statement: NTIS	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 126
	20. Security Class (This Page) UNCLASSIFIED	22. Price $6.00 2.25

FINAL REPORT

EVALUATION OF THE CONTROLLABILITY OF SO_2 EMISSIONS FROM COPPER SMELTERS IN THE STATE OF ARIZONA

by

I.J. WEISENBERG
G.E. UMLAUF

Environmental Engineering Dept.
(A. Stein, Director)

JUNE 1975

EPA CONTRACT NO. 68-02-1354: Task 8

Project Officer: PHILLIP WONDRA
Chief, Pacific-Inland Plans Section
Air Programs Branch
Air and Hazardous Materials Division
Region IX EPA
San Francisco, California

PACIFIC ENVIRONMENTAL SERVICES, INC.
1930 14th Street
Santa Monica, California 90404

TABLE OF CONTENTS

		Page
I.	INTRODUCTION AND SUMMARY	I-1
II.	GENERAL CONSIDERATIONS	II-1
	A. EMISSION POINTS	II-1
	B. SULFUR BALANCE SUMMARY	II-3
	C. RETROFIT CONTROL TECHNIQUES FOR ARIZONA SMELTERS	II-5
III.	REVIEW OF CURRENT SMELTER OPERATIONS	III-1
	A. GENERAL	III-1
	B. INDIVIDUAL SMELTERS	III-3
	1. PHELPS DODGE/MORENCI	III-3
	a. Smelter and Pollution Control Systems	III-3
	b. Sulfur Balance, Flows, Temperatures	III-6
	c. Present SO_2 Control System and its Capability	III-6
	d. Present Smelter Control System Modification Plans	III-7
	2. PHELPS DODGE/DOUGLAS	III-7
	a. Smelter and Pollution Control Systems	III-7
	b. Sulfur Balance, Flows, Tempertures	III-10
	c. Present SO_2 Control System and its Capability	III-10
	d. Present Smelter and Control Systems Modification Plans	III-10
	3. AMERICAN SMELTING AND REFINING CORP/HAYDEN	III-10
	a. Smelter and Pollution Control Systems	III-10
	b. Sulfur Balance, Flows, Temperatures	III-15
	c. Present SO_2 Control System and its Capability	III-15
	d. Present Smelter and Control System Modification Plans	III-15
	4. MAGMA COPPER COMPANY/SAN MANUEL	III-16
	a. Smelter and Pollution Control Systems	III-16
	b. Sulfur Balance, Flows, Temperatures	III-19
	c. Present SO_2 Control System and its Capability	III-20
	d. Present Smelter and Control System Modification Plans	III-20

TABLE OF CONTENTS (continued)

		Page
IV.	REVIEW AND SUMMARY OF AVAILABLE AND POTENTIALLY AVAILABLE SO_2 EMISSION CONTROL SYSTEMS AND TECHNIQUES	IV-1
	A. INTRODUCTION	IV-1
	1. Available Control Systems	IV-1
	2. Potentially Available Control Systems	IV-1
	3. Market Factors	IV-2
	B. SULFURIC ACID PLANT TECHNOLOGY	IV-3
	1. System	IV-3
	2. Conditioning of SO_2 Gas	IV-3
	3. Conversion of SO_2 to SO_3 and Absorption	IV-7
	4. Operating Problems	IV-11
	5. Effectiveness of Acid Plant for SO_2 Control on Copper Smelters	IV-12
	C. SO_2 CONCENTRATION SYSTEMS	IV-14
	1. Sodium Sulfite Scrubbing System	IV-14
	2. Magnesium Oxide (MgO) Scrubbing System	IV-15
	3. Dimethylaniline (DMA) and Xylidine Scrubbing Systems	IV-16
	4. Ammonia Absorption System (Cominco Process)	IV-16
	D. REDUCTION OF SULFUR DIOXIDE TO FORM ELEMENTAL SULFUR	IV-17
	E. OXYGEN ENRICHMENT	IV-18
	1. CHEMISTRY	IV-18
	2. SMELTING	IV-19
	3. OXYGEN ADDITION	IV-20
	a. In Reverberatory Furnace	IV-20
	b. Converters	IV-27
	c. Roasters	IV-28
	4. OXYGEN COST AND AVAILABILITY	IV-29
	F. SCRUBBER SYSTEMS RESULTING IN WASTE PRODUCTS	IV-31
	G. LIQUID SO_2/ACID PLANT	IV-32
	H. CONCLUSION	IV-32
V.	REVIEW OF POSSIBLE SO_2 CONTROL APPROACHES FOR EACH SMELTER	V-1
	A. INTRODUCTION	V-1

TABLE OF CONTENTS (continued)

		Page
B.	ASSUMPTIONS AND GROUND RULES FOR PREPARING ALTERNATIVE CONTROL TECHNIQUES	V-1
C.	INDIVIDUAL SMELTERS	V-4
1.	REVIEW OF POSSIBLE CONTROL APPROACHES FOR PHELPS DODGE/MORENCI	V-4
2.	SUMMARY OF ALTERNATIVES FOR PHELPS DODGE/ MORENCI	V-12
3.	REVIEW OF POSSIBLE CONTROL APPROACHES FOR PHELPS DODGE/DOUGLAS	V-12
4.	SUMMARY OF ALTERNATIVES FOR PHELPS DODGE/ DOUGLAS	V-17
5.	REVIEW OF POSSIBLE CONTROL APPROACHES FOR AMERICAN SMELTING AND REFINING CORP. (ASARCO/HAYDEN)	V-17
6.	SUMMARY OF ALTERNATIVES FOR AMERICAN SMELTING AND REFINING CORP. (ASARCO/HAYDEN)	V-24
7.	REVIEW OF POSSIBLE CONTROL APPROACH FOR MAGMA COPPER COMPANY/SAN MANUEL	V-25
8.	SUMMARY OF ALTERNATIVES FOR MAGMA COPPER COMPANY/SAN MANUEL	V-28
LIST OF REFERENCES		VI-1
APPENDIX A	Copper Smelting Process	A-1
APPENDIX B	Visits to Arizona Copper Smelters and Arizona Department of Health	B-1
APPENDIX C	Alternative Control Plans, Operating Conditions, and Cost Estimate Calculations	C-1

LIST OF FIGURES

		Page
FIGURE 1.	COPPER BEARING MATERIAL	II-2
FIGURE 2.	RETROFIT SO_2 CONTROL TECHNIQUES FOR EXISTING EQUIPMENT AT ARIZONA SMELTERS	II-6
FIGURE 3.	PROCESS FLOW SHEET: PHELPS DODGE/MORENCI . . .	III-4
FIGURE 4.	PROCESS FLOW & SULFUR BALANCE SHEET: PHELPS DODGE CORP/DOUGLAS	III-8
FIGURE 5.	PROCESS FLOW & SULFUR BALANCE SHEET: ASARCO/ HAYDEN	III-11
FIGURE 6.	PROCESS FLOW & SULFUR BALANCE SHEET: MAGMA COPPER CO/SAN MANUEL	III-17
FIGURE 7.	GAS COOLING REQUIRED FOR PRODUCTION OF 93% OR 98% H_2SO_4	IV-5
FIGURE 8.	EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONVERSION OF SULFUR DIOXIDE TO SULFUR TRIOXIDE.	IV-8
FIUGRE 9.	SINGLE AND DOUBLE CONTACT SULFURIC ACID PLANT SCHEMATIC	IV-9
FIGURE 10.	REVERBERATORY FURNACE FLAME TEMPERATURES . . .	IV-21
FIGURE 11.	REVERB SMELTING WITH TONNAGE OXYGEN	IV-24
FIGURE 12.	REVERB PRODUCTION AND FLUE GAS DEPENDENCE UPON TONNAGE OXYGEN AND FUEL	IV-25
FIGURE 13.	REVERB SMELTING	IV-26
FIGURE 14.	POWER REQUIREMENTS FOR TONNAGE OXYGEN PLANTS. DAILY PRODUCTION VS. POWER REQUIREMENTS . . .	IV-30
FIGURE 15.	COST OF SULFURIC ACID PLANTS	V-5
FIGURE 16.	ACID PLANT VOLUME FLOW RATE VS. ACID CAPACITY .	V-6

LIST OF TABLES

		Page
TABLE 1.	ARIZONA COPPER SMELTERS SULFUR BALANCE SUMMARY . .	II-4
TABLE 2.	ALTERNATIVE CONTROL PLANS - PHELPS DODGE/MORENCI .	V-8
TABLE 3.	ALTERNATIVE CONTROL PLANS - PHELPS DODGE/DOUGLAS .	V-13
TABLE 4.	ALTERNATIVE CONTROL PLANS - ASARCO/HAYDEN	V-19
TABLE 5.	ALTERNATIVE CONTROL PLANS - MAGMA/SAN MANUEL . . .	V-26

I. INTRODUCTION AND SUMMARY

The objective of this study was to conduct smelter inspections and engineering analyses of existing, planned, available or potentially available SO_2 control systems in support of preparation of regulations for copper smelters in the Arizona portion of Region IX. The inspections and analyses were to assess the 1) feasibility of upgrading existing or planned permanent controls, 2) feasibility of operational changes to improve control, and 3) applicability of available or potentially available constant emission control technology.

This report includes smelter process description, operating conditions, emission estimates, and control system performance evaluation. The evaluation includes consideration of all factors bearing on the practical application of available and potentially available technology including pollutant removal efficiency, operational reliability, space requirements, installed equipment and cost.

A total of seven copper smelters in the State of Arizona were reviewed. All installations were evaluated for fugitive emissions; four for available or potentially available control technology for the overall process. The latter four were Phelps Dodge/Morenci; Phelps Dodge/Douglas; Magma/San Manuel and ASARCO/Hayden. The other three included Kennecott/Hayden; Inspiration/Miami and Phelps Dodge/Ajo.

There is a wide range of difference between the smelters in terms of their present and future planned SO_2 control capability. On the one hand, one of the smelters is completely eliminating its older process, particularly the reverberatory furnaces and has installed an electric furnace and Hoboken converters providing the potential for nearly complete SO_2 control. At the other extreme one smelter presently has no constant SO_2 control whatsoever. The other smelters fall somewhere within this range in terms of SO_2 control capability.

The major source of uncontrolled SO_2 emissions at the present time in the average smelter is the reverberatory furnace since most smelters control converter offgases. The reason for this is that the furnace offgases do not contain sufficiently high SO_2 concentration (minimum 3.5% to 4%) to send directly to a sulfuric acid plant which is the most conventional

approach to capturing SO_2. There are several systems that appear attractive for controlling the SO_2 from a reverberatory furnace, but these are considered potentially available requiring some additional full scale operational experience before they would be considered as presently available. In all cases however, control alternatives have been included in this report and are shown in tabular form for each smelter.

Alternate control techniques are discussed in general as applied to each specific smelter. It should be specifically noted that these techniques includes both potentially available as well as available methods. The summary data includes the source of the SO_2 within the smelter, the additional acid plant capacity required, the stream characteristics in terms of percent SO_2 and volume flow, the requirement for a preheater, the requirement for a concentrator, the total sulfur captured, the total sulfur escaping, the expected total installed cost estimate and the estimated time schedule for installation of the equipment.

II. GENERAL CONSIDERATIONS

A. EMISSION POINTS

The typical copper smelting process consists of the charge mixing and handling step, followed by roasting (in some cases), smelting, converting and finally refining. The flow diagram shown in Figure 1, shows the major copper smelting steps with conventional equipment as used in most Arizona smelters. (Reference 1).

SO_2 generation does not occur until heat has been applied to the sulfur-bearing charge material; this first takes place in the roasters. Those smelters using roasters employ either a multiple hearth or liquid bed design. While the multiple hearth roaster theoretically is capable of producing a relatively high SO_2 (up to 8.0%) stream concentration, in the actual case of the smelters using this equipment the stream is extremely SO_2 lean (1.8% to 2.5%), almost equivalent to that leaving a reverberatory furnace. The main reason for occurrence of the lean stream in actual practice is the age of the equipment and the large number of leakage points, allowing dilution air to enter the system. Fluid bed roasters produce a rich SO_2 (10.2% to 11.3%) stream capable of being processed directly in a sulfuric acid plant.

Up until 1974, all copper smelters in Arizona used reverberatory furnaces as the primary smelting equipment. These furnaces either received calcines from the roasters or took "green charge" directly from the charge preparation area. SO_2 stream concentration from .5 to 1.5% is generally produced by smelters with reverberatory furnaces. The reasons for the lean stream include dilution by the following:

- Air which can enter from many points throughout the reverberatory furnace
- Gases generated from the combustion of fuels
- The large amount of nitrogen resulting from the air used for combustion of the fuel
- Water vapor in the case of "green charge"

Those smelters using roasters appear to generate a lower average SO_2 concentration from the reverberatory furnaces. This can be explained by the fact that calcines from the roaster have had a significant amount of sulfur removed.

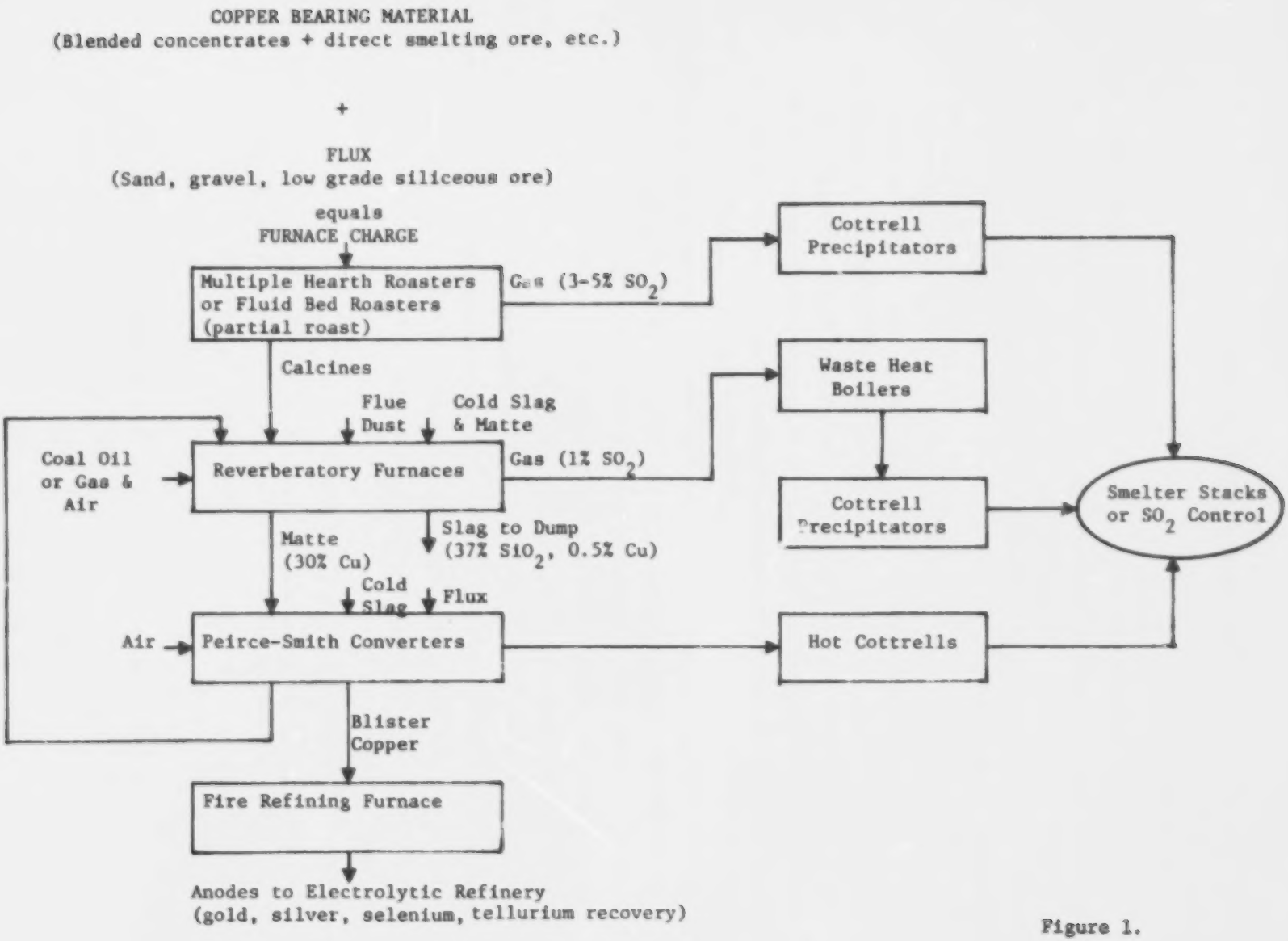

COPPER BEARING MATERIAL
(Blended concentrates + direct smelting ore, etc.)
+
FLUX
(Sand, gravel, low grade siliceous ore)
equals
FURNACE CHARGE
Multiple Hearth Roasters or Fluid Bed Roasters (partial roast)
Gas (3-5% SO_2)
Cottrell Precipitators
Calcines
Waste Heat Boilers
Flue Dust
Cold Slag & Matte
Coal Oil or Gas & Air
Reverberatory Furnaces
Gas (1% SO_2)
Cottrell Precipitators
Smelter Stacks or SO_2 Control
Matte (30% Cu)
Slag to Dump (37% SiO_2, 0.5% Cu)
Cold Slag
Flux
Air
Peirce-Smith Converters
Hot Cottrells
Blister Copper
Fire Refining Furnace
Anodes to Electrolytic Refinery
(gold, silver, selenium, tellurium recovery)

Figure 1.

Matte, normally containing 30%to 40% copper leaves the reverberatory furnace and is transported by open ladle to the converters. Here, the matte is refined to blister copper of 97%to 98% purity. Offgas streams from the converters may contain 6%to 8% SO_2 stream concentration; this gas is capable of being processed directly in a sulfuric acid plant.

The blister copper from the converters is then sent to a refining furnace, where it encounters a reducing atmosphere to further eliminate the small remaining percentage of sulfur and other impurities. Essentially no SO_2 is generated at this point.

Thus, the major points where SO_2 is emitted are the roasters, reverberatory furnaces, and converters. Fugitive emissions are generated primarily from the points at which the hot material (slag or molten-copper-containing material) is transferred from major processing equipment to the next processing area.

B. SULFUR BALANCE SUMMARY

A comparison between smelters in Arizona for sulfur emissions, total sulfur generated for each major piece of equipment, solids (slag and wastes), and fugitive emissions is shown in Table 1. The input sulfur is the amount of sulfur contained in the feed to the smelting system. It is roughly proportional to the production rate of the smelter.

Variation in SO_2 concentration from the roasters is extreme, ranging from 1.8% to 11.3%. This is primarily related to the equipment, with the low percentage streams issuing from the multiple hearth roasters and the high percentage from the fluid bed roasters.

Reverberatory furnace stream concentration varies from 0.4% to 1.5% SO_2. As mentioned in the preceding section, this is caused by the large amount of dilution air, as well as the nitrogen supplied with the air for combustion. Note that those smelters employing roasters generally have a lower SO_2 content in the reverberatory furnace gases because a significant portion of the sulfur is eliminated in the roasters before the charge reaches the furnace.

The converter SO_2 stream concentration generally ranges from 4.4% to 6.5% (average). In the single case where 1.8% is encountered, poor hooding allowing a considerable amount of dilution air to enter the system prevents

Table 1. ARIZONA COPPER SMELTERS SULFUR BALANCE SUMMARY[1]

Smelter	Input Sulfur (TPD-S)	Roaster		Reverb		Converter		Slag and Solid Waste (TPD-S)	Fugitive[2] Emissions (TPD-S)	Present Sulfur Captured (TPD-S)
		%SO_2 b.v.	TPD-S	%SO_2 b.v.	TPD-S	%SO_2 b.v.	TPD-S			
Magma/San Manuel	954	-	-	1.5	259	5.5	660.9	34.0	0.1	681.8
Phelps Dodge/ Douglas	777.1	1.8	349.9	1.1	122.1	1.8	245.7	22.0	31.4	22.0
Asarco/ Hayden[3]	551.3	2.5	138	0.7	99	4.7	302	12.3	-	207.3
Phelps Dodge/ Morenci	981.2	11.3	175.1	0.9	273.1	6.5	492.9	23.1	17.0	668.4
Kennecott/ Hayden	345	10.2	164	0.4	32	4.4	141	5	3	312
Phelps Dodge/ Ajo	203	-	-	1.5	68	5.4	120	5	10	183
Inspiration/ Miami[4]	235	-	-	.25[5]	44	1.5[5]	159	11.7	20.3	11.7

1. Data considered as representative averages only. Approximate date January, 1975 except as noted.
2. Not measured directly - can include accumulated errors.
3. Based on 1974 data (5 months) @ 1800 TPD submitted to the State of Arizona - Fugitive emissions not reported.
4. Old System - now replaced with electric furnace, Hoboken converters and acid plant.
5. Large amount of dilution.

higher concentrations. Hooding which is currently being installed should increase this percentage. Slag and tailings sulfur captured is a relatively small percentage of total sulfur, varying from 1.5% to 3.6% of the input sulfur.

Fugitive emissions data contain considerable scatter. This is partly attributable to the difficulty in measuring this quantity, which in many instances is taken by difference. The difference determination will result in the inclusion of all measurement errors in this factor. In general, 5% fugitive emissions seemed to be the consensus of the industry.

C. RETROFIT CONTROL TECHNIQUES FOR ARIZONA SMELTERS

This analysis is limited to "available" and potentially available" retrofit control methods for SO_2. The term available is defined for this report as that equipment and those processes which have been used for some period of time (nominally one year) in an actual smelter operating under full scale production conditions, with satisfactory results. Other techniques have been considered and are noted to require some additional experimental development work at the final full-scale operating smelting conditions. These are considered "potentially available". Processing equipment changes have not been included as available or potentially available retrofits, even though they may be an effective means of achieving emission reductions.

Figure 2 is a summary of the retrofit SO_2 control techniques for Arizona smelters considered in this study. This chart is divided into strong stream and weak stream control equipment because of the major effect of this factor on control equipment selection.

The most applicable SO_2 control system used extensively in the copper smelting industry is a sulfuric acid plant. The SO_2 streams emanating from the smelters are converted to sulfuric acid. Generally, a single contact sulfuric acid plant has been used in the range of stream concentrations from 3.5% to 7%. This type of acid plant normally operates at efficiencies of 96.5% to 97.5% within the range of tail gas SO_2 concentration of 2,000 ppm to 2,600 ppm. The double contact sulfuric acid plants can be used in the range from 5.5% to 11% SO_2 stream concentration, and normally operate at efficiencies in the range of 98.5% to 99.5% and approximately 500 ppm to 650 ppm tail gas SO_2 concentration.

Problems occur in applying sulfuric acid plants to copper smelters because the smelter tends to produce a fluctuating stream, both in

RETROFIT SO_2 CONTROL TECHNIQUES FOR EXISTING EQUIPMENT AT ARIZONA SMELTERS

AT ARIZONA SMELTERS

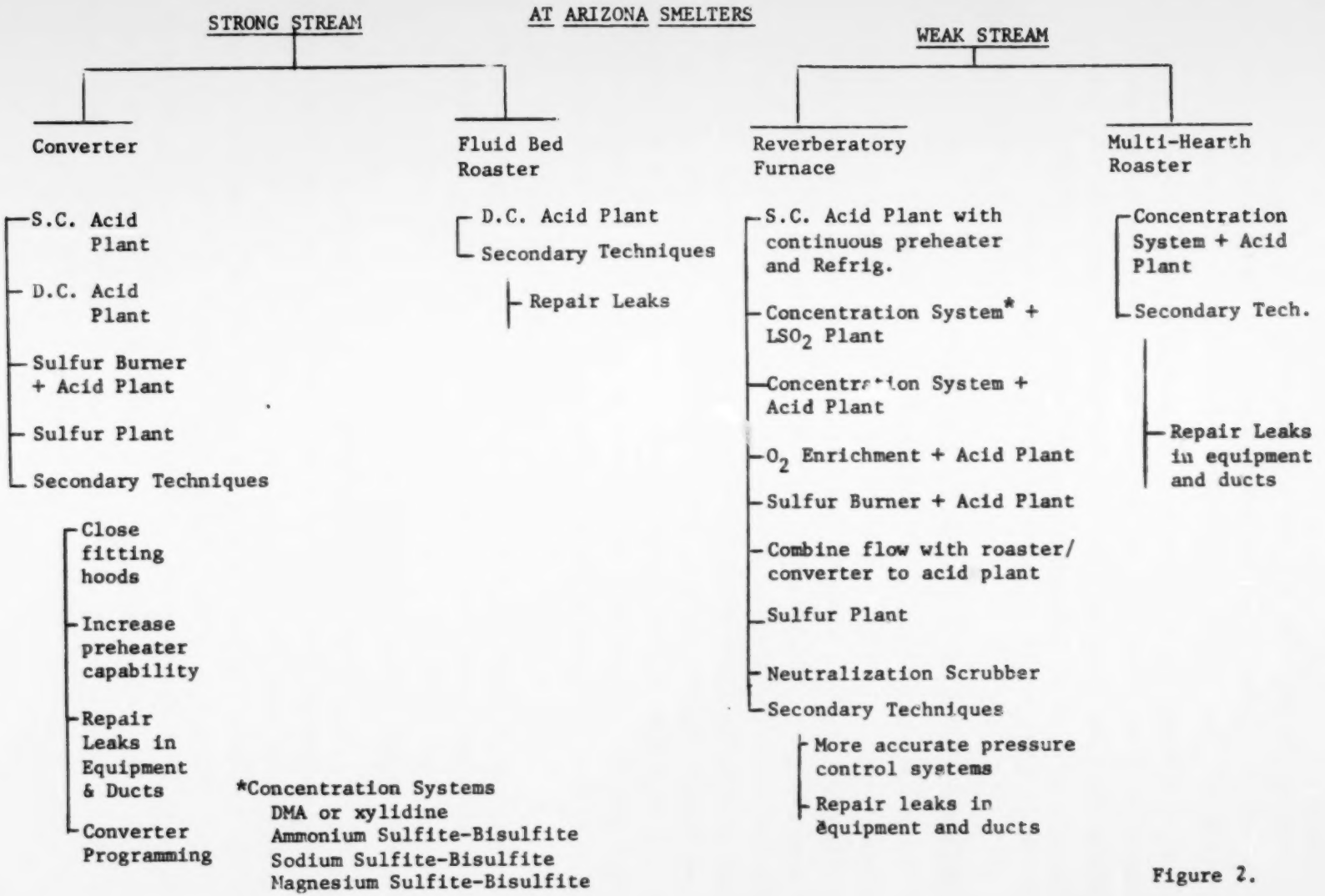


Figure 2.

concentration and quantity, and the sulfuric acid plant requires a steady constant stream for optimum operation. Additional demonstrated techniques are available to correct these problems. These include providing a sulfur burner for makeup SO_2, constant preheater operation to maintain converter efficiency at low concentrations, and refrigeration to reduce water buildup at low SO_2 concentrations. The refrigeration technique has been demonstrated down to 1.0% SO_2 concentration. Initial capital outlay and operating costs are always higher when using the latter techniques. This analysis also includes available secondary techniques such as closely fitting hoods, increasing preheater capabilities, and repairing of leaks in equipment and ducts.

The concentration systems (scrubbing with an absorption medium) as well as oxygen enrichment are considered to be techniques requiring additional testing and development. Concentration systems use a material such as dimethylaniline to absorb the SO_2. It is then passed to a regeneration system where the SO_2 is driven off in a concentrated stream which may be between 85% and 100% SO_2. These gases may be used either to enrich a lean stream from a roaster or reverberatory furnace or to liquify the sulfur dioxide for storage and future use or sale.

Oxygen enrichment is the technique wherein oxygen is mixed with the process air for reverberatory furnaces or converters, allowing an increase in production rate as well as in the concentration of SO_2. 4% SO_2 and higher has been generated in full scale reverberatory furnaces with oxygen addition. Once the 4% level has been reached, these gases can be used directly in a sulfuric acid plant. Gases which may be extremely rich, such as those from a roaster, can be combined with lean gases in certain special cases to produce a gas stream strong enough to be used directly in an acid plant.

Control of fugitive emissions is an extremely difficult task requiring special hooding and ventilation systems along with good maintenance practices and leak elimination.

Additional discussion of SO_2 control techniques is provided in Section IV.

III. REVIEW OF CURRENT SMELTER OPERATIONS

A. GENERAL

A detailed background description of the copper smelting processes and industry may be found in Reference 2. It is assumed, for purposes of this report, that the reader has access to this document; therefore, only a minimum of discussion of copper smelting is included here. See Appendix A.

Current operations and SO_2 control of existing copper smelters in Arizona vary considerably, lepending on the operating management, material being processed and existing equipment. At one extreme, one smelter is introducing new equipment to completely change its processing. This will allow essentially complete collection of SO_2 emissions. At the other extreme, one smelter has no SO_2 collection equipment.

Table 1 summarizes the sulfur emitted from the major equipment (roasters, reverberatory furnaces and converters) for seven Arizona smelters. Even though Inspiration Copper is currently in the startup phase of basically new equipment (electric furnace and Hoboken converters) the data from their old conventional plant has been included for comparison purposes. The table shows the weight in tons per day of sulfur generated by each of these pieces of equipment at various plants, and the concentration of the SO_2 in the off-gas stream.

There is a wide variation in the percentage of SO_2 coming from the roasters from different smelters, primarily because some have multiple hearth roasters and some the fluid bed type. The multiple hearth roasters tend to be very old, and have a large number of leakage points which allow dilution air to enter and mix with the main offgas stream, thereby reducing the SO_2 percentage. This would indicate that if roasters are used, the fluid bed design would be preferable from an SO_2 collection standpoint, although there is evidence to indicate that a multihearth design in good condition can generate at least 4% SO_2 stream concentration.

The need for roasting depends in part, on the sulfur content of the copper concentrates. With the higher sulfur content there is more of a tendency to use roasters. In addition, the roaster provides flexibility when there is a wide variation in the sulfur content, such as may be encountered by custom smelters.

Most conventional reverberatory furnaces generate offgas streams in the range of 0.5% to 1.6% SO_2. Where there is a roaster in the system, the amount of SO_2 generated in the reverberatory furnace is a smaller percentage of the total generated. Because of the weak SO_2 stream and the large volume flow rate, only one smelter in Arizona is attempting to collect reverberatory furnace SO_2 by the use of a concentration system.

The converters generate SO_2 with a wide range of concentrations because they are essentially an intermittent or batch type operation. Most smelters have relatively tight fitting converter hoods designed to collect offgases during the blowing period. In all smelters, there are at least two converters and in some cases as many as eight. These converters can be programmed to generate the rich SO_2 stream consecutively thereby maintaining a relatively constant rich stream which can then be passed to the acid plant.

Generally during slag blowing 15% SO_2 offgases are generated and during copper blowing 21% SO_2 is generated. Usually if there are no hoods present the dilution air entering the duct above the mouth of the converter will reduce SO_2 concentration to 1.5%to 5%. With the use of tight fitting hoods over the converter mouth, it is possible to obtain final diluted 5-8% SO_2 in slag blowing and 10-13% SO_2 during copper blowing. With proper programming of several converters, it is possible to minimize the batch type operation effect and maintain a reasonably constant SO_2 percent offgas going to the acid plant. However, proper programming of converters is difficult in actual practice.

In the case of the Inspiration Copper smelter the new converters are a different design (Hoboken) which provides for complete offgas collection during the entire converting process. This reduces the fugitive emissions compared to the conventional Peirce-Smith Converter. In addition, the Inspiration electric furnace theoretically allows collection of all SO_2 generated in the smelting process because it produces a gas stream which can be fed to an acid plant. The rich stream is created as a result of the major gas volume reduction due to elimination of combustion requirements and the sealed enclosure minimizing dilution.

The following sections will review each of the four individual smelters considered for overall control in this study. These sections describe the smelter, its sulfur balance and operating conditions, the present SO_2 control system and capability, and future smelter modification plans.

B. INDIVIDUAL SMELTERS

1. Phelps Dodge/Morenci

a. Smelter and Pollution Control Systems

The process flow is shown schematically in Figure 3.

A fluid bed roaster is capable of handling 35% of the total plant feed and the rest goes directly as green charge to the reverberatory furnaces. The roaster requires a special feed which is very fine, 6-10 mesh maximum size range. No recycle material is put through the roaster. Approximately 84% of total roaster charge is concentrate. There are four old reverberatory furnaces and one new furnace that has been completed and is currently being started up. Two of the furnaces receive calcine feed from the roaster and the remaining three receive green charge. One furnace may handle either green or calcine feed. Furnaces No. 1 and No. 2 burn 175,000 SCFH and No. 3 and No. 4 burn 165,000 SCFH of gaseous fuel.

Reverberatory furnace No. 5 will generate a total of 240,000 SCFM of which 140,000 SCFM is gas produced by the burners and from the feed. The remainder is dilution air entering from openings in the furnace walls and roof. 1.2% SO_2 concentration is expected from No. 5 offgas. Dilution also occurs in the other reverberatory furnaces and can be expected to be higher percentage of the total gas as indicated in Table 1. No more than four furnaces can be operated at one time because converter capacity is not sufficient to handle more.

Each of the old reverberatory furnaces has 4 matte tap holes and one slag tap hole. The new No. 5 furnace has five matte tap holes and two slag tap holes. Only four matte tap holes will normally be used. All of the matte tap holes for the No. 5 furnace are enclosed in a room. The hole punching machine is also enclosed in this room which is then vented to the collection system. This minimizes fugitive emissions and appears to be a promising approach.

Considerable heat leaves the furnace roofs. The heat loss depends upon the insulation qualities of the refractory brick. No. 5 roof is limited to 15" thick magnesite brick because of structural considerations.

The reverberatory furnaces are normally operated at negative pressure of 0.5 to .01 inches w.c. Charging takes place approximately every hour for a period of about two minutes and tends to produce positive internal pressures

Typical values - large deviations can be encountered

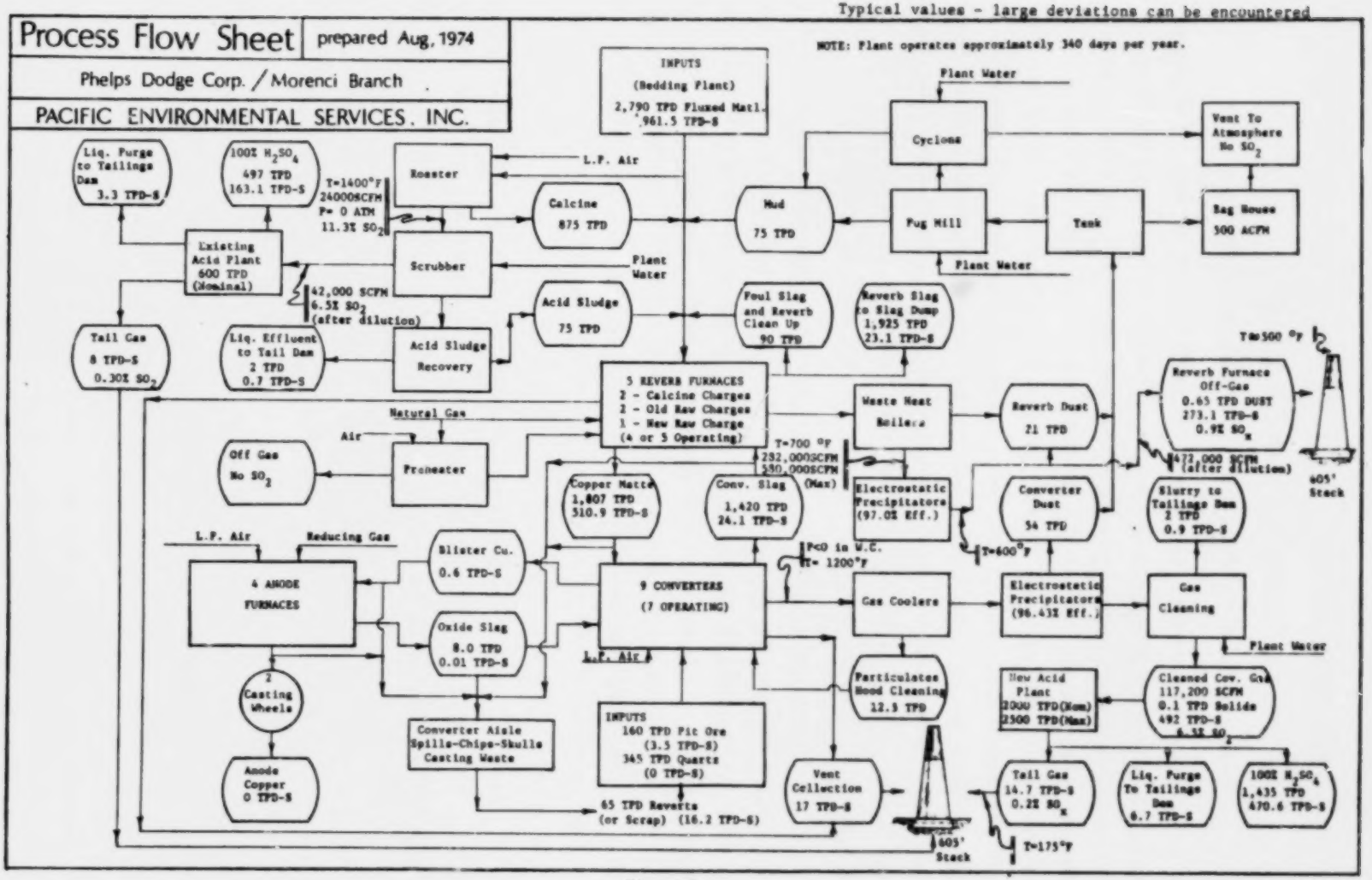

Process Flow Sheet
prepared Aug, 1974
Phelps Dodge Corp. / Morenci Branch
PACIFIC ENVIRONMENTAL SERVICES, INC.
NOTE: Plant operates approximately 340 days per year.
INPUTS (Bedding Plant) 2,790 TPD Fluxed Matl. 961.5 TPD-S
Plant Water
Cyclone
Vent To Atmosphere No SO2
Liq. Purge to Tailings Dam 3.3 TPD-S
100% H2SO4 497 TPD 163.1 TPD-S
T=1400°F 240005CFM P= 0 ATM 11.3% SO2
Roaster
L.F. Air
Calcine 875 TPD
Mud 75 TPD
Pug Mill
Tank
Bag House 500 ACFM
Existing Acid Plant 600 TPD (Nominal)
Scrubber
Plant Water
42,000 SCFM 6.5% SO2 (after dilution)
Acid Sludge 75 TPD
Foul Slag and Reverb Clean Up 90 TPD
Reverb Slag to Slag Dump 1,925 TPD 23.1 TPD-S
Plant Water
Tail Gas 8 TPD-S 0.30% SO2
Liq. Effluent to Tail Dam 2 TPD 0.7 TPD-S
Acid Sludge Recovery
5 REVERB FURNACES 2 - Calcine Charges 2 - Old Raw Charges 1 - New Raw Charge (4 or 5 Operating)
Waste Heat Boilers
Reverb Dust 21 TPD
T=500 °F
Reverb Furnace Off-Gas 0.65 TPD DUST 273.1 TPD-S 0.9% SOx
472,000 SCFM (after dilution)
605' Stack
Natural Gas
Air
Off Gas No SO2
Preheater
T=700 °F 232,000SCFM 250,000SCFM (Max)
Copper Matte 1,807 TPD 510.9 TPD-S
Conv. Slag 1,420 TPD 24.1 TPD-S
Electrostatic Precipitators (97.0% Eff.)
Converter Dust 54 TPD
Slurry to Tailings Dam 2 TPD 0.9 TPD-S
T=600°F
L.F. Air
Reducing Gas
4 ANODE FURNACES
Blister Cu. 0.6 TPD-S
9 CONVERTERS (7 OPERATING)
P<0 in W.C. T= 1200°F
Gas Coolers
Electrostatic Precipitators (96.4% Eff.)
Gas Cleaning
Plant Water
Oxide Slag 8.0 TPD 0.01 TPD-S
L.F. Air
Particulates Hood Cleaning 12.3 TPD
New Acid Plant 2000 TPD(Nom) 2500 TPD(Max)
Cleaned Conv. Gas 117,200 SCFM 0.1 TPD Solids 492 TPD-S 4.5% SO2
2 Casting Wheels
Converter Aisle Spills-Chips-Skulls Casting Waste
INPUTS 160 TPD Fit Ore (3.5 TPD-S) 345 TPD Quartz (0 TPD-S)
Vent Collection 17 TPD-S
Tail Gas 14.7 TPD-S 0.2% SOx
Liq. Purge To Tailings Dam 6.7 TPD-S
100% H2SO4 1,435 TPD 470.6 TPD-S
Anode Copper 0 TPD-S
65 TPD Reverts (or Scrap) (16.2 TPD-S)
605' Stack
T=175°F

Figure 3

resulting in an increase of fugitive emissions. Fugitive emissions are currently being encountered from the furnace waste heat boilers and uptake system.

The new No. 5 furnace cannot take calcines because it is fed by a rubber belt. The new furnace burner capability is not sufficient to operate at maximum furnace capacity. Preheated air must be used to make up the additional 15% heat generation capacity required to meet the design. This production capacity still has to be proven. The older furnaces do not use preheated air. The new furnace uses Hauck burners capable of burning any fuel from natural gas to No. 6 fuel oil. The burners are all automatic and can be adjusted to place the flame at optimum position in relation to the charge. Automatic chute return of the slag is provided. This chute enters the furnace during feeding and is withdrawn when not in use. This minimizes fugitive emissions.

A total of eight Peirce-Smith converters are installed and operating with the ninth nearing completion. With this large number of converters the average number of converters blowing is 3.37 when seven units are active. This can provide a relatively even SO_2 stream quantity and concentration to the acid plant. Close fitting hoods are used for all the converters. Hood pressure is maintained by a series of damper controls. Both a plug damper to completely shutoff the converter hood when not blowing and an opposed blade damper for volume and system balancing control are employed in the exhaust system for each unit. Remote closed circuit television is used to survey the uncollected emissions from the converter. Damper controlled reduction of hood pressure is used to eliminate uncollected emissions.

Gases from the roaster go through a series of cyclones and then to a 500 ton per day acid plant. Gases from the converters pass through a cleaning system then to a 2500 ton per day (maximum) new acid plant.

The old acid plant handling roaster offgas, produces approximately 500 TPD and has a maximum capacity of 600 TPD. It was built in 1965. Approximately 150 TPD of acid is used in the plant and the remainder sold. Operating time on the acid plant averages 21 hours per day. A feed stream of 6.5% SO_2 is obtained by diluting the roaster offgas. A 3000 Hp blower is used to move acid plant gas at 18,000 to 24,000 SCFM.

The new 2500 TPD sulfuric acid plant built by Chemico is a single contact design. It has been designed so that it is possible to add a double

contact circuit.

The new acid plant gas conditioning system consists of a humidifying tower, cooling tower, packed tower, precipitator, and drying tower followed by the remainder of the plant. Parallel gas systems are used after the initial hot gas precipitator immediately downstream from the smelter. Thus, the major portion of the acid plant is in two trains allowing independent operation of each side.

A preheater can be used to operate one side of the system to allow acid production even when gas stream concentration is as low as 2.5% SO_2. The plant is designed to make 93% acid using 6.5% SO_2.

Acid plant blowers deliver 89,000 ACFM at 110°F with a suction pressure of 11.3 PSIA and a discharge pressure of 17.7 PSIA. Acid plant tail gas is estimated to be 328,700 ACFM at 175°F.

Average yearly operating days for this smelter is 350.

b. Sulfur Balance, Flows, Temperatures

The process flow sheet shown in Figure 3 indicates sulfur and material rates. Gas volume flow rates, temperatures and output SO_x (as SO_2) per cent are also indicated. Table 1 shows sulfur emitted at various points throughout the system.

c. Present SO_2 Control System and its Capability

The 600 TPD acid plant used to process roaster offgas produces an offgas stream of approximately 0.2% SO_2 calculated using the data obtained from the smelter.

The new 2500 TPD (maximum) acid plant does not yet have performance data well established. Using the data provided by the smelter, 1,435 TPD of 100% H_2SO_4 is produced from the converter offgas. This indicates additional capacity is available, or that the system is capable of handling wide fluctuations in input.

The greatest source of uncontrolled emissions for this smelter is from the reverberatory furnaces. If the feed to the smelter is as shown in the process flow sheet, then there is sufficient acid plant capacity to handle the 92,854 TPY of sulfur presently passing from the reverberatory furnaces to the stack. This is equivalent to 836 TPD of acid which, if added to the

1,435 TPD still falls below the maximum capability of the plant which is 2500 TPD for short periods. However, discussion with the smelter personnel indicates that they expect peak loads from the converters alone to generate capacity feed gas to the plant.

d. Present Smelter Control System Modification Plans

With the new No. 5 reverberatory furnace, the new No. 9 converter and the new 2500 TPD acid plant in their startup phases, there are no immediate plans for additional modifications to plant or process.

2. Phelps Dodge/Douglas

a. Smelter and Pollution Control Systems

The Phelps Dodge/Douglas copper smelter system consists of 24 multi-hearth roasters receiving green feed and supplying calcines to three reverberatory furnaces that supply matte to five converters. Two anode furnaces are used for refining and supply copper for anode casting. (See Figure 4 for flow sheet). One holding furnace is also used as required. Precipitators are used for particulate control from each of the major components; roasters, furnaces and converters. No equipment is available and no attempt is made to control SO_x emissions. All gases, after passing through the precipitators go to a stack and are emitted to the atmosphere.

Feed to the Douglas Smelter consists of approximately 40-70% ore from Phelps Dodge in Bisbee or Tyrone as well as custom ore from the Cypress-Pima mines. Mostly custom ore is expected in the future.

Of the total of 24 Hirschoff Multi-hearth roasters installed only 18 are usually operating at one time. These are very old units in poor condition. Because of considerable leakage they are a source of fugitive emissions. In addition, the calcines drop from the roaster discharging to a railcar located below the hoppers. This is a source of considerable fugitive dust and gas emissions.

The Phelps Dodge/Douglas smelter has three reverberatory furnaces; one side wall charge with a basic hung or floating roof and two batch charge with sprung arch silica roofs. Each furnace has four matte tap holes and one slag tap hole. The sidewall charge furnaces have open ports on the top for feeding. These open holes are plugged with mud for sealing, but do not

Typical values - large deviations can be encountered

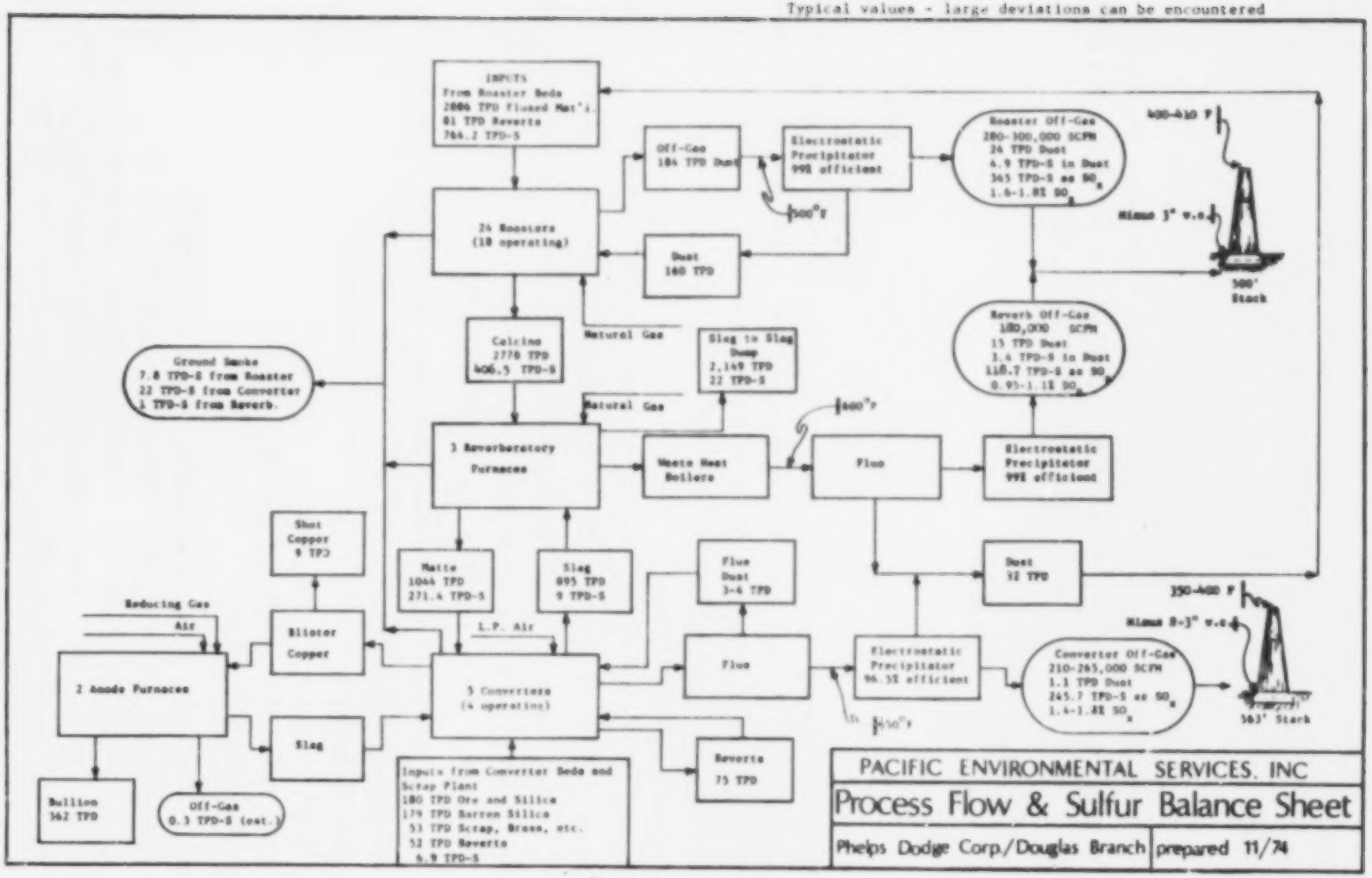


Figure 4

always get plugged, resulting in the generation of fugitive emissions. A 40% copper matte is obtained from the reverberatory furnace.

Hooding and covering the matte slag tap holes and launders is presently planned. However, the one example noted, which was a slag tap hole, had swinging doors located close around the opening. It did not appear that this was a practical solution to the problem.

To repair the furnace roof a slurry is prepared and air sprayed through pipe nozzles onto the brick work. This is done during operating of the furnace and no shutdown for repair is required.

There are a total of four operating converters with one additional for standby or repair status. The converters are the conventional Peirce-Smith type, 13 foot diameter by 30 foot long.

Air to the converters is as follows:

Slag blow 20,000 to 25,000 SCFM
Copper blow 20,000 to 22,000 SCFM

Installation of close fitting hoods on the converters is now in process. However, the hood design, which is of the Walter radiation cooled type, does not fit close to the top of the converters. There is a gap approximately one foot high along the front of the converter. It was stated that this is for dilution air and observation of the flame for process control. Smelter personnel estimate that additional dilution air is approximately 120% of the gases leaving the converter.

One converter flux and revert feed system is being changed to include an enclosed rubber belt conveyor system to minimize fugitive emissions. The feed will go through a hole in the side of the close fitting hood. This is currently under development.

Auxiliary oxygen is used to produce additional heat in the converters when they have a fairly large percentage of reverts.

The stack is 500 feet high and approximately 21 feet average diameter. The 21 feet is measured at 200 feet above ground. There are no forced draft fans in the air or gas handling system. They simply use the stack draft which is approximately minus 2-3 inches w.c. at the stack.

b. Sulfur Balance, Flows, Temperatures

The flow sheet, Figure 4 and the sulfur balance summary Table 1 include sulfur balance, flows, temperatures and SO_2 concentration. A major portion, 45% of the sulfur is released in the roasters with the second largest amount, 32% from the converters.

Offgases from the roaster are claimed to contain 1.6%to 1.8% SO_x and offgases from the converters are claimed to contain 1.4%to 1.8% SO_x. These are very low values and indicate extensive in leakage and dilution.

c. Present SO_2 Control System and its Capability

There is no SO_2 removal system at this smelter.

d. Present Smelter and Control Systems Modification Plans

There are no present smelting system modification plans.

Two new baghouses are presently being installed in the screening area for particulate removal. Each has 40,000 ACFM capacity. A new precipitator to handle the reverberatory furnace offgases and a new precipitator to handle the roaster offgases are being installed also for particulate removal. The new precipitators are expected to be 99 + % efficient. New flues will be installed from the reverberatory furnaces and the roasters.

Hooding and covering of the matte and slag tap holes and launders is planned to minimize emissions. There will be burners placed in the ducts from the ground smoke ventilation system in order to keep above the dew point.

The areas where the calcines are dropping from the roasters will be semi enclosed to minimize air motion.

There are no present SO_2 control system installation plans.

3. American Smelting and Refining Corp./Hayden

a. Smelter and Pollution Control Systems

The smelter system is shown on flow sheet, Figure 5.

Multiple hearth roasters are used to supply feed for conventional reverberatory furnaces which provide the converter charge. 25% of the input sulfur is removed from the feed in the roasters. 18% of the input

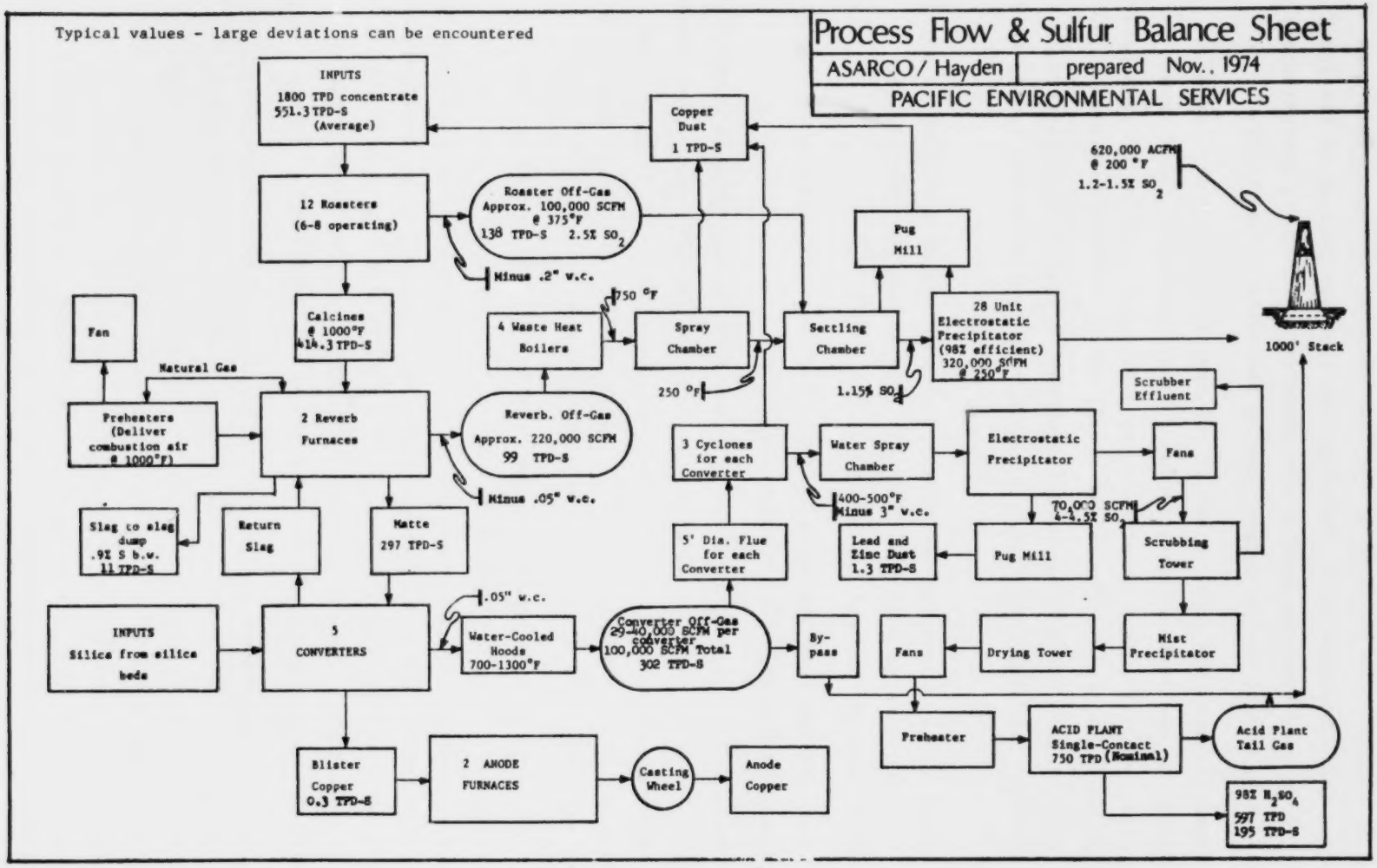

Typical values - large deviations can be encountered
Process Flow & Sulfur Balance Sheet
ASARCO / Hayden
prepared Nov., 1974
PACIFIC ENVIRONMENTAL SERVICES
INPUTS
1800 TPD concentrate
551.3 TPD-S
(Average)
Copper Dust
1 TPD-S
620,000 ACFM
@ 200 °F
1.2-1.5% SO2
12 Roasters
(6-8 operating)
Roaster Off-Gas
Approx. 100,000 SCFM
@ 375°F
138 TPD-S 2.5% SO2
Minus .2" w.c.
Pug Mill
Fan
Calcines
@ 1000°F
414.3 TPD-S
750 °F
4 Waste Heat Boilers
Spray Chamber
Settling Chamber
28 Unit Electrostatic Precipitator
(98% efficient)
320,000 SCFM
@ 250°F
1000' Stack
Natural Gas
Preheaters
(Deliver combustion air @ 1000°F)
2 Reverb Furnaces
Reverb. Off-Gas
Approx. 220,000 SCFM
99 TPD-S
250 °F
1.15% SO2
Scrubber Effluent
Minus .05" w.c.
3 Cyclones for each Converter
Water Spray Chamber
Electrostatic Precipitator
Fans
Slag to slag dump
.9% S b.w.
11 TPD-S
Return Slag
Matte
297 TPD-S
400-500°F
Minus 3" w.c.
70,000 SCFM
4-4.5% SO2
5' Dia. Flue for each Converter
Lead and Zinc Dust
1.3 TPD-S
Pug Mill
Scrubbing Tower
.05" w.c.
INPUTS
Silica from silica beds
5
CONVERTERS
Water-Cooled Hoods
700-1300°F
Converter Off-Gas
29-40,000 SCFM per converter
100,000 SCFM Total
302 TPD-S
By-pass
Fans
Drying Tower
Mist Precipitator
Preheater
ACID PLANT
Single-Contact
750 TPD (Nominal)
Acid Plant Tail Gas
Blister Copper
0.3 TPD-S
2 ANODE FURNACES
Casting Wheel
Anode Copper
98% H2SO4
597 TPD
195 TPD-S

Figure 5

sulfur is removed from the feed in the reverberatory furnace. This goes either to the atmosphere or to the slag. Fifty-seven percent of the input sulfur is removed from the feed to the converters. There is approximately .2% sulfur by weight in the copper leaving the casting department.

Precipitators are used to remove the dust from the roaster gases, converters and the reverberatory furnace. They operate at 250°F input temperature because ASARCO experience has shown that this is the temperature at which they get maximum precipitator efficiency. ASARCO completed a 1000-foot tall stack in March 1974 and all equipment offgases from roasters, reverberatory furnaces, converters and acid plant are presently fed to this stack.

There are 12 roasters, normally 6-8 of them are in operation at any one time. A flapper valve located at the top of each roaster controls the pressure within the roaster to a minus .1 to .2 inch w.c.

The calcines from the roaster are dropped through a slag gate onto a railcar. Fugitive emissions are low at this point.

The roaster offloading of the calcines into calcine cars is accomplished by opening a slide gate and dropping the material into the car. When loading the calcines a puff of gas will be generated when the valve is open. The calcines are at approximately 1000°F. After loading, the car is then moved to the charging floor of the reverberatory furnaces.

Volume flow from one large roaster is 20,000 SCFM at 375°F. The smaller roasters handle 15,000 SCFM. Stack draft is used for most of the roasters. However, a booster fan has been added to handle gas flow from the last five roasters to help balance the system. Gases from the roasters are combined with reverberatory furnace gases and they are then passed into a 28 unit precipitator. Dampers are used to control the flow. Roaster gases entering the precipitator are at 250°F and at approximately 2.5% SO_2.

A hopper is used to collect the material from the roasters and this is then fed by a Wagstaff gun into the reverberatory furnace. The gun is a 2 ft. diameter waterjacketed cylinder that causes the material to flow into the furnace when vibrated. Firing is reduced to 25% when loading the furnace to maintain negative pressure and minimize fugitive emissions. It takes 2-3 minutes to drop a charge into the furnace and this is done at approximately 20 minute intervals.

There are three charge points on one furnace and four charge points on the other reverberatory furnace. Each furnace operates with side wall charging. One furnace is 26 feet wide and 110 feet long, and the other is 15 feet wide and 30 feet long. Silica sprung arch roofs are used. Normal operating pressure is minus .05" w.c., however, it appears that during the loading and at some other times there are positive pressure surges within the furnace (even though the firing rate is reduced during loading).

Preheaters are used to preheat the air for the reverberatory furnace. There is one slag tap hole and four matte tap holes for each furnace. Slag from the reverberatory furnaces containing .9% sulfur, by weight, is sent to the dump.

Fuel gas consumption for the reverberatory furnaces is 140,000 ACFH at 60°F to number 2 and 110,000 ACFH to number 4.

Gases from the reverberatory furnace pass into a waste heat boiler and are reduced in temperature to leave at approximately 750°F. From the waste heat boiler the gases enter a spray chamber where 100 GPM of water is sprayed into the gases to reduce the temperature to 250°F. From the spray chamber the gases are combined with roaster gases passed through a settling chamber and into a cottrell precipitator chamber at 250°F. Total gas flow including roaster gases going to the cottrell is approximately 500,000 ACFM at 250°F. From the precipitator the gases then go to the stack.

ASARCO has designed a moving hood over the ladles for the matte tapping. This hood comes down on a hinge and completely covers the ladle. There are several small square openings in the hood to allow the operator to determine the level in the ladle. This is an effective approach for minimizing fugitive emissions from ladles containing molten material.

There are five converters, two 13 feet in diameter by 30 feet long and three 13 feet in diameter by 33 feet long. One of the smaller units is soon to be replaced by a larger one.

Generally four ladles are used to load a converter which contains approximately 80 tons per charge. Maximum matte concentration is 55% copper with normal concentration in the 40-42% range. Slag from the converters is returned to the reverberatory furnace. There are two slag return launders.

Converter air including both blowing air and dilution air varies from 29,000 - 40,000 SCFM. Each converter hood has two dampers one a bullseye

or complete shutoff damper and the other a multi-blade damper for pressure control. There are three fans located in parallel in the converter hood circuit. The multi-blade dampers are adjusted to maintain negative .05" w.c. at the converter hood. The fans provide plus 1" w.c. at the control before going to the bypass.

Gases from the converter hoods which are water cooled along the side and have radiation cooled doors, pass either to the acid plant or around the bypass to the stack. Hood temperatures range from 700°F to 1800°F. The gases drop in temperature going through the high velocity flue from the hoods by approximately 300°F. They reach about 400° - 500°F at the downstream cyclones where maximum of 650°F may be seen. Pressure at the cyclones is -3" w.c.

Each converter has a 5 ft. diameter flue which transports the gases to three cyclones, a water spray chamber, an electrostatic precipitator consisting of four parallel units of three sections each, two gas scrubbing and cooling towers in parallel trains of one open and one packed tower, a mist precipitator consisting of four units of two sections each, drying tower and the single contact acid plant. Normally 4-4.5% SO_2 is contained in the gases going to the acid plant.

A 750 TPD rated sulfuric acid plant processes gases from the converter hoods only. This plant was designed in 1968 and started up in 1971. The plant produced 182,989 tons of acid in 1972 and 117,386 tons acid in the ten months period for 1973. The plant is capable of making clear commercial grade sulfuric acid at either 98% or 94% concentration. It was claimed by ASARCO that the plant emits 2000 PPM at an entrance gas of 4.12% SO_2.

Considerable difficulties are and have been encountered with the plant. It is a Chemiebau plant designed and installed by Rust Engineering. The acid plant was down the entire month of October and two weeks in November in 1973.

The acid plant has a preheater. A preheater is needed when the SO_2 in the gas stream reaches 3%. Operation of the plant can continue if the gas stream concentration goes to zero for a period of 15 minutes without turning on the preheater. Beyond this point they recirculate a small amount of gas particularly when all converters are out. There are two acid plant blowers in parallel that are on continuously.

ASARCO is presently shipping acid to Southern California due to lack

of local markets.

b. Sulfur Balance, Flows, Temperatures

The flow sheet, Figure 5, and the sulfur balance summary Table 1 include sulfur balance, flows, temperatures and SO_2 concentration. Over half of the sulfur, 55%, is released in the converters with 25% the next largest amount, released from the roasters.

Only 2.5% SO_2 concentration is obtained from the roasters indicating excessive input of dilution air because of the many leakage points in the equipment. The 4% to 4.5% SO_2 emitted from the converters indicates normal concentration and capability of processing directly in a single contact acid plant.

The 620,000 ACFM leaving the stack indicates additional dilution air entering the gas handling system at some point before reaching the stack.

c. Present SO_2 Control System and Its Capability

Gases from the converter pass to a single contact sulfuric acid plant with capacity in the 600 TPD to 750 TPD range. This is not of sufficient size to capture the total amount of sulfur leaving the converters. A total acid plant capacity of 907 TPD is required. In addition, smelter personnel indicated that this plant is in very poor condition and is not operable an inordinately large part of the time because of the excessive maintenance required. Currently (May, 1975) work is being done to allow complete collection of converter SO_2 in the existing acid plant by the end of 1975.

d. Present Smelter and Control System Modification Plans

ASARCO is currently reviewing methods for minimizing fugitive emissions at furnace tap points and launders. They are reworking several converter hoods to obtain improved capture. Gas cooling system modifications in the acid plant to minimize fugitive emissions and downtime are also in progress.

There are no firm additional SO_2 control system installation or modification plans at present.

4. Magma Copper Company/San Manuel

a. Smelter and Pollution Control Systems

The Magma/San Manuel smelter consists of three reverberatory furnaces with five converters currently, and a sixth to be added shortly. A seventh may be added at a later date if the need is indicated when the sixth is placed in operation. The Magma compliance plan contains detailed data on the operation of the system and is reflected in the smelter flow sheet Figure 6. Operation at a concentrate feed range of from 800,000 - 1,125,000 tons per year is possible.

The gases from the reverberatory furnace pass through a waste heat boiler, electrostatic precipitator and then out the stack. No SO_2 collection is attempted. Gases from the converters pass up through water cooled hoods to electrostatic precipitators, then to scrubbing towers and a Monsanto single contact acid plant designed with the capability of modification to double contact. Blister copper from the converters is taken to the anode furnace where it is further refined and cast into anodes for final electrolytic refinement.

Initial copper concentrate contains approximately 28% copper. This is fed to three natural gas or oil fired side charge reverberatory furnaces all 102 ft long by 32 ft, 34 ft and 36 ft wide respectively. The reverberatory furnaces have suspended roofs with sealing material such as steel wool, mud or asbestos packed along the joint. The roof is anchored with tie rods suspended from the ceiling.

Magma normally operates two of the reverberatory furnaces at full capacity at all times. The third reverberatory furnace may be operated from one fourth to full capacity (currently three fourths). The reverberatory furnace uses side wall feed along the front 40% length of the furnace. Two air preheaters capable of operating on either No. 2 fuel oil or natural gas are used to preheat the air going to the burners of the reverberatory furnace. This allows an increase in the gas temperature and also combustion efficiency. It is necessary to have at least 60% fire to the reverberatory furnace to maintain temperature. This is some indication of the amount of induction air being used, Magma is presently operating on approximately a four year life for the brick before rebricking is required.

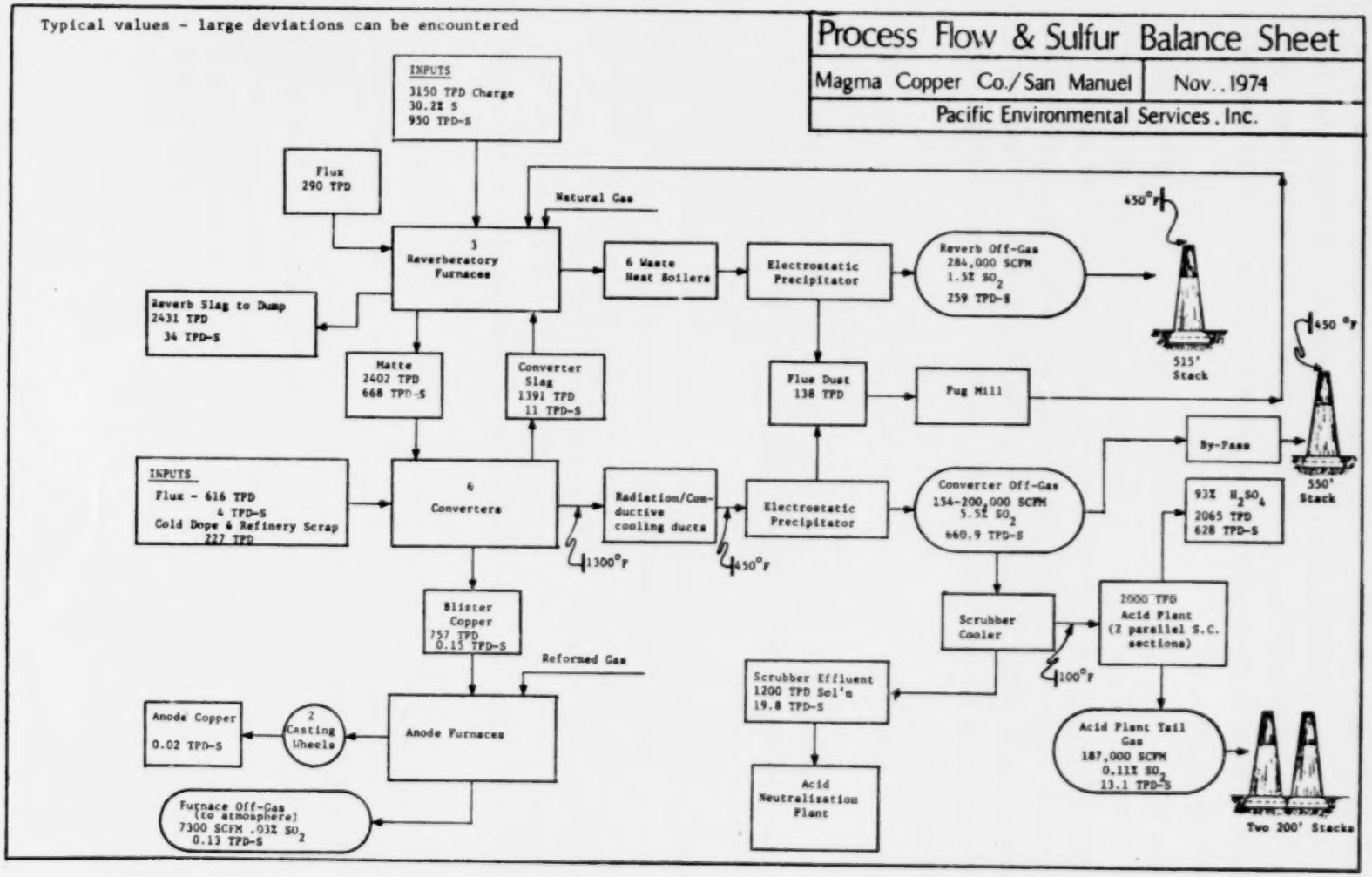

Typical values - large deviations can be encountered
Process Flow & Sulfur Balance Sheet
Magma Copper Co./San Manuel
Nov., 1974
Pacific Environmental Services, Inc.
INPUTS
3150 TPD Charge
30.2% S
950 TPD-S
Flux
290 TPD
Natural Gas
3
Reverberatory
Furnaces
6 Waste
Heat Boilers
Electrostatic
Precipitator
Reverb Off-Gas
284,000 SCFM
1.5% SO_2
259 TPD-S
450°F
515'
Stack
Reverb Slag to Dump
2431 TPD
34 TPD-S
Matte
2402 TPD
668 TPD-S
Converter
Slag
1391 TPD
11 TPD-S
Flue Dust
138 TPD
Fug Mill
450 °F
By-Pass
550'
Stack
INPUTS
Flux - 616 TPD
4 TPD-S
Cold Dope & Refinery Scrap
227 TPD
6
Converters
Radiation/Conductive
cooling ducts
Electrostatic
Precipitator
Converter Off-Gas
154-200,000 SCFM
5.5% SO_2
660.9 TPD-S
93% H_2SO_4
2065 TPD
628 TPD-S
1300°F
450°F
Blister
Copper
757 TPD
0.15 TPD-S
Scrubber
Cooler
2000 TPD
Acid Plant
(2 parallel S.C.
sections)
Reformed Gas
100°F
Scrubber Effluent
1200 TPD Sol'n
19.8 TPD-S
Anode Copper
0.02 TPD-S
2
Casting
Wheels
Anode Furnaces
Acid Plant Tail
Gas
187,000 SCFM
0.11% SO_2
13.1 TPD-S
Furnace Off-Gas
(to atmosphere)
7300 SCFM .03% SO_2
0.13 TPD-S
Acid
Neutralization
Plant
Two 200' Stacks

FIGURE 6.

Magma controls the reverberatory furnace process by adjusting draft, fuel input, fuel to air ratio and feed scheduling.

The matte which contains 32-35% copper, is processed in three 13' x 32.5' and two 15' x 35' Peirce-Smith type converters. Converter slag is returned to the reverberatory furnace and blister copper is delivered to four anode holding furnaces where it is blown and cooled prior to casting into 785 lb. anodes.

The 15 x 35 foot converter uses an air supply varing from 30,000-45,000 SCFM. Scheduling of the converters to maintain a more or less constant flow of SO_2 to the acid plant must be done. A single charge will remain in the converter for a period of about 14 hours. There are three or more slag blows of about 1½ hours each and one finish blow. Oxygen has been used up to 30 TPD at times in converter blowing air to increase cold dope treatments.

Water cooled hoods over the converters pick up most of the gaseous effluent. However, in some cases there is leakage at the end of the converters. This is particularly true when the converters are operated at a high temperature condition. The ends are held to the sealing surface by spring loaded tie rods.

The gases leave the converter collection system and enter a long radiation/conduction cooler which simply consists of a duct sized to provide 7,000 FPM gas velocity. Total gas flow from the converters varies from 154,000 - 200,000 SCFM. At this range of flow the gases are cooled from an inlet of 1200 - 1400°F down to 400-500°F out of the cooler. They then pass into a precipitator which removes a major portion of the particulate.

The converter gases going to the acid plant contain approximately 5.5% SO_2. Magma expects to fix 625 TPD of sulfur in the acid plant with 13.2 TPD sulfur emitted from the acid plant.

The 2000 TPD acid plant (rated) has just been completed (January 1975) and is in the process of being started up. From the precipitator the gases pass to two packed towers that have weak acid flowing through to provide cooling and humidification. From the coolers the gas which will be at a maximum temperature of 140°F and usually 100°F, will pass to the mist precipitators. Six mist precipitators are in the parallel series circuit.

From the mist precipitators the gases pass to the dryer where the moisture is absorbed in concentrated acid. The gases then pass to the SO_2 to SO_3 converter which has four conventional stages with three interstage heat exchangers that use the incoming gas to cool the outgoing gas.

One special feature of this plant is that there are two parallel trains starting downstream of the hot gas precipitator and following through to the end of the acid plant. This design can allow shutdown of one side for maintenance while the other side continues to operate.

In addition, each side has a preheater that is designed to operate continuously. The preheater will control the temperature coming out of the converter. Thus, if the concentration of SO_2 in the gas stream is too low for autogenous operation the burner will immediately and automatically turn on providing sufficient heat for efficient conversion. The burner is completely automatic and will stop and start on the temperature signal from the converter.

Carbate heat exchangers are used for cooling the acid. In addition, a teflon spaghetti cooler is used for cooling the weak acid. An air cooled evaporation cooling tower is used to cool all cooling water.

Another interesting feature of the system is that Fiberglass Reinforced Plastic (FRP) is used throughout to handle the gases up to the dryer. There are three main blowers for the acid system with one being used as a spare. Each blower has a 6000 Hp motor and its own pressurized lubrication system.

Magma also has built a neutralization plant which uses the tailings mixed with the acid. Their tailings are basic, and therefore, they do have a major portion of the material to neutralize the acid. They also must add lime rock. This plant is presently being used when the total amount of acid produced cannot be sold or exceeds storage capacity. Up to 600 TPD has been neutralized.

b. Sulfur Balance, Flows, Temperatures

The flow sheet, Figure 6 and the sulfur balance summary Table 1 include sulfur balance, flows, temperatures and SO_2 concentration. 69% of the sulfur input is released at the converters. The average SO_2 concentration in the converter offgas is 5.5% and is suitable for acid plant processing. 27% is released from the reverberatory furnace.

c. Present SO_2 Control System and Its Capability

The present 2000 TPD single contact acid plant is new and is sized to handle the total amount of converter offgas. At 97% efficiency approximately 67% of the total input sulfur would be captured. The remaining sulfur passes out the stack or into the atmosphere as fugitive emissions. This acid plant was designed to allow modification to a double contact system.

d. Present Smelter and Control System Modification Plans

An extensive particulate and SO_2 control program is nearing completion at this smelter. The addition of a sixth converter is also nearing completion. A possible seventh may be added at some future date if required.

There are no present plans to control the SO_2 generated by the reverberatory furnaces, representing the only major uncontrolled points in this smelter.

IV. REVIEW AND SUMMARY OF AVAILABLE AND POTENTIALLY AVAILABLE SO_2 EMISSION CONTROL SYSTEMS AND TECHNIQUES

A. INTRODUCTION

Methods for control and recovery of sulfur dioxide emissions from smelters can for convenience be placed in four categories according to the nature of the sulfur product:

1. Systems producing sulfuric acid,
2. Systems producing concentrated sulfur dioxide, either for use as such or as an intermediate in production of some other material, such as sulfuric acid or elemental sulfur,
3. Systems producing elemental sulfur,
4. Systems producing "throwaway" products.

1. Available Control Systems

Most experience in SO_2 control for copper smelters has been with capture by conversion to sulfuric acid. This has been accomplished as early as the 1920's and is possible because of the rich (above 4%) SO_2 streams issuing from roasters and converters. This is the most readily available approach for SO_2 control.

Processes converting SO_2 to sulfur are available. Sulfur is considered easier to ship and store than sulfuric acid. However, all sulfur production processes require the use of a reducing agent which is usually a fuel, natural gas or coal. With the current energy problem it is believed that fuel availab'lity and cost will inhibit the production of sulfur from smelter offgases.

2. Potentially Available Control Systems

Lean SO_2 streams (0.5% to 1.5%) from reverberatory furnaces have rarely been captured and usually are passed to atmosphere. While it is possible, under certain conditions, to operate a sulfuric acid plant under very low concentration conditions (1.0%), the initial and operating costs are increased.

Concentration of lean streams has been accomplished by using an

absorptive medium and then regenerating to obtain an 80% to 100% SO_2 stream that can be liquified or mixed with other gases to adjust concentration for acid plant use.

Neutralization or so called "scrubber" systems are being introduced extensively for use in power plant SO_2 control. Power plant emissions can be in the same range of SO_2 concentration as from primary smelter reverberatory furnaces. The copper smelter industry has not used neutralization as a primary control technique. At least three factors may effect the use of direct neutralization systems for the Arizona smelters. These factors are:

1. The effect of gas stream impurities that are significantly different and may be greater than encountered in power plants.
2. Availability of water for the slurry systems.
3. The physical/chemical characteristics and economics of disposing of the waste products.

Since questions on the effect of these factors remains largely unanswered, this study has not included the technique as a possible alternative approach. Furthermore, even though neutralization is considered an available control technique in the power plant industry, it would still be considered in the "potentially available" category for copper smelter reverberatory furnaces.

Oxygen enrichment of input air used in reverberatory furnaces and converters can increase SO_2 concentration to the point of direct use in a sulfuric acid plant. While this technique requires additional testing at each individual smelter, data available indicate it to be a potentially available approach to increasing stream concentration with a minimum cost.

While Reference 2 includes many of these control approaches, the following sections B through H discuss significant points relating each of the techniques to the Arizona smelters.

3. Market Factors

With the increase in sulfuric acid production capability in the State of Arizona as a result of smelter pollution control efforts, marketing can become more of a problem unless the economy is operating at a high level as occurred in 1974. The Cominco smelter in Canada encountered the same problem in the 1920's and eventually resolved it by introducing additional processes that could use the sulfuric acid as an intermediate. This led to production

of ammonium phosphate fertilizer, ammonium nitrate, liquid fertilizer, urea, potash, ammonium sulphate fertilizer, phosphate and liquid SO_2. Thus, it has been demonstrated that an operating smelter can set up to use (rather than neutralize and waste) sulfuric acid produced as a result of pollution controls even though it may be difficult to sell directly. Obviously each smelter must consider the product path depending on local conditions. While no U.S. smelters are known to have attempted this approach (except for liquid SO_2) it falls within the same category as introducing waste heat boilers to use, rather than waste, a useful byproduct. Uses for sulfuric acid, particularly in agriculture, are increasing rapidly. Direct application on alkaline and clay soils has been found to be beneficial in Arizona and California and should open up extensive local markets.

Sulfur, as mentioned above, is an alternate product to sulfuric acid but requires a reducing agent (fuel) which introduces additional costs. Again, this still may be a desireable route because of the easier storability and shipping requirements as compared to sulfuric acid. Local market conditions and reductant availability would determine if this route is feasible.

B. SULFURIC ACID PLANT TECHNOLOGY

1. System

The process for the manufacture of sulfuric acid from copper smelter offgases* consist of three principal steps, namely:

- Purification of the sulfur dioxide (SO_2) gas from the smelter.
- Conversion of the sulfur dioxide (SO_2) gas to sulfur trioxide (SO_3) gas.
- Absorption of the sulfur trioxide (SO_3) in sulfuric acid (H_2SO_4).

2. Conditioning of SO_2 Gas

Smelter gas can normally contain combinations of SO_2, metallic fume, dust, SO_3 and gaseous impurities. The SO_2 gas stream entering the acid plant must be clean and dry to minimize operational problems.

The gas is usually cooled in passing through a waste heat boiler or other heat exchanger sufficiently to enter a precipitator for major

*See Schematic Figure 9.

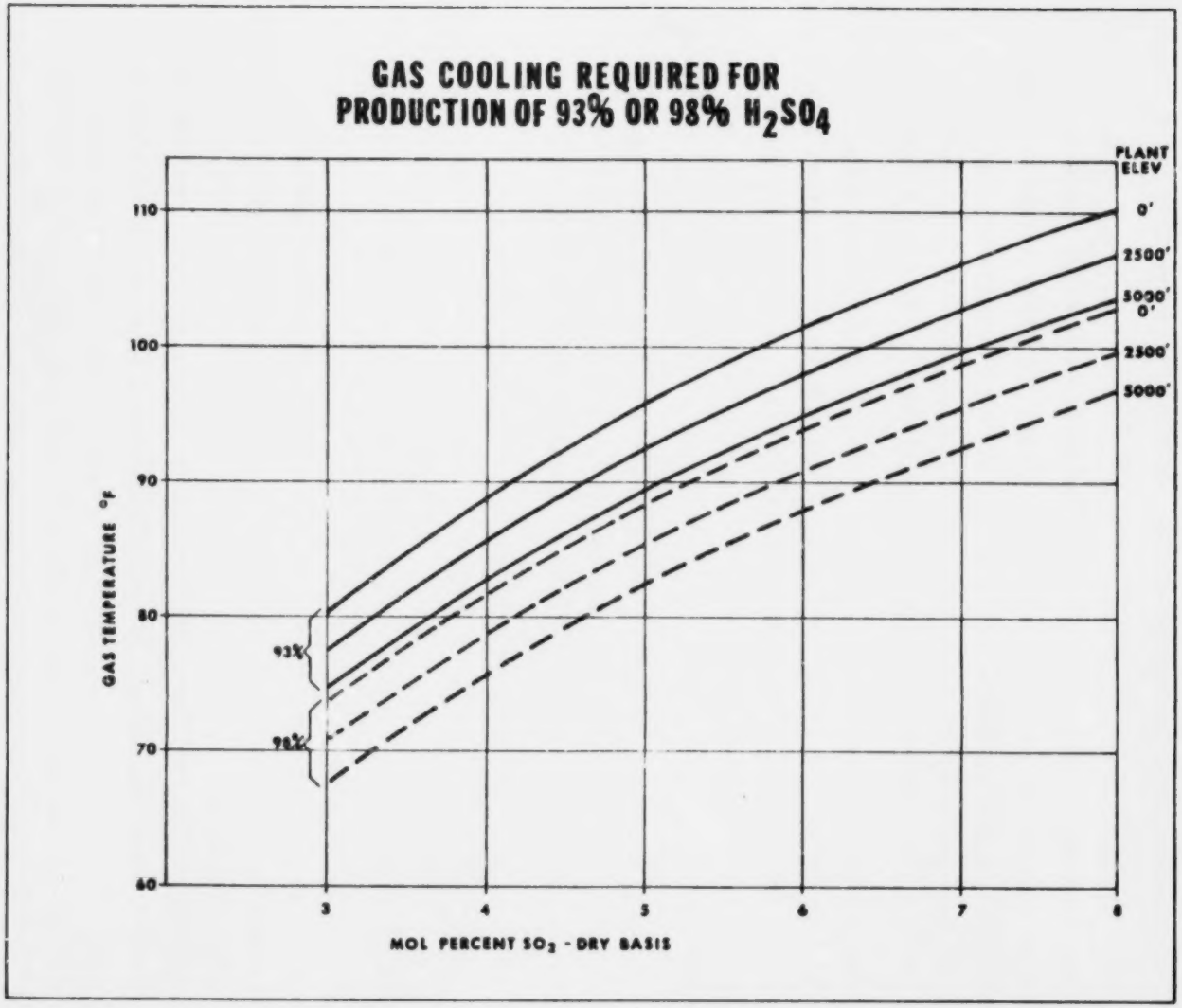
particulate removal. The gases then pass to a spray chamber or cooling tower where water removes many of the remaining impurities and further cools the gas. Scrubber equipment has also been used for this purpose.

The gas must be cooled to reduce its moisture content. Final cooled temperature is determined by the SO_2 concentration, product acid strength desired and the elevation of the plant above sea level. This characteristic can be seen in Figure 7 showing gas cooling required for production of 93% or 98% H_2SO_4 versus mole percent SO_2 on a dry basis. An allowance has been made in these curves to permit the addition of some water to the strong acid system to provide more flexible control of acid strength. Shell and tube type gas coolers can be used for final cooling to 100°F or less.

The water discharged from the spray chamber or cooling tower will contain the impurities removed from the gas and will also be saturated with SO_2 from the gas. To recover sulfur values and reduce effluent nuisance, this water may be passed through a stripping column where a stream of air removes most of the SO_2 from the water. The SO_2 gas so recovered is fed back to the tower. The water from the stripping column then may be either neutralized or discharged.

The gas leaving the cooling section is passed through a mist precipitator in which most of the remaining particles of acid mist, metallic fume and dust are removed by electrostatic precipitation. Sulfuric acid mist generally contains particles less than 5 microns and is very difficult to remove from the gas stream except with an electrostatic precipitator. If this mist is allowed to enter the contact section of the acid plant it will cause corrosion problems in carbon steel ducts, heat exchangers and the main blower.

The usual mist precipitator is a tube type with vertical tubes 6-10" in diameter made of lead. High voltage discharge electrodes are suspended in the center and run the entire length of the tubes. The mist particles are attracted to the tube walls, flow downward and are collected in the lower header in the form of 5-10% H_2SO_4. Two mist precipitators installed in series can provide 99% removal efficiency. The reason for two precipitators is because the entrained acid in the gas stream tends to produce arcing and requires a reduced input voltage lowering the efficiency of the unit. With two units in series the voltage is reduced only to the first unit so the overall efficiency is affected only slightly. In many cases,



Reference 10

Figure 7

only one precipitator is used to minimize capital expenditures.

The gas passes from the mist precipitator to the drying tower where it moves up through a bed counter current to the flow of 93% acid. The acid absorbs whatever moisture is present and the gas is dried to a maximum water vapor content of 5 mg/SCF. The heat generated by the absorption of water in the circulating acid is removed in heat exchangers cooled with water reducing acid temperature to approximately 105°F.

For high SO_2 to SO_3 conversion efficiency the converter entrance gas should contain at least 1.3 volumes of oxygen for every volume of sulfur dioxide. This ratio maximizes the gas strength at the converter and determines the required volume of gas handled per ton of sulfuric acid produced. It is normally controlled by introducing additional air to supply oxygen.

The main gas blower usually follows the drying tower to provide sufficient suction to pull the air required through the purification system and sufficient pressure to blow the gas through the converter heat exchanger system and the absorption tower. Blower static pressure capability is typically 150" w.c.

The gas leaves the blower at about 130°F and flows through a series of heat exchangers in which its temperature is raised to 820°F, the required temperature for entering the first catalyst layer in the converter.

The dry gas leaving the blower passes through the shell side of three (usually) shell and tube heat exchangers in series in which its temperature is raised to 820°F. In the cold heat exchanger, the SO_2 gas is heated to approximately 480°F as it flows counter-current to the SO_3 gas leaving the converter. In the intermediate exchanger, the SO_2 gas is further heated to about 555°F by cooling the gas leaving the second bed of the converter. Further heating of the SO_2 gas to 820°F is accomplished in the hot, or converter, heat exchanger by cooling the partially converted gas leaving the first catalyst bed from about 1075°F to 820°F. Suitable by-passers are provided around these exchangers to permit maintaining optimum temperatures to the converter. An SO_3 cooler utilizing forced air may also be provided to further cool the SO_3 gases leaving the cold heat exchanger before they enter the absorption tower. Operation of the plant can be maintained with any of the three heat exchangers blanked and taken out of service by the use of the SO_3 cooler for heating the SO_2 gas and the introduction of quench sulfur dioxide gas at strategic points for temperature adjustment.

3. Conversion of SO_2 to SO_3 and Absorption

The conversion of SO_2 to SO_3 takes place in the converter. The converter contains several layers of a vanadium pentoxide catalyst, the purpose of which is to accelerate the reaction between SO_2 and oxygen to form SO_3. The converter is normally of the three stage four bed type, designed to provide maximum conversion efficiency.

The heat of reaction generated in the first stage of conversion where 70-75% of the SO_2 reacts with O_2 in the gas stream is removed from the gas in the external converter heat exchanger. The temperature rise may be 250-300°F. The rise in temperature reduces the conversion equilibrium. See Figure 8. The partially converted gas, cooled to 820°F in the converter heat exchanger, is returned to the second stage. The heat of reaction in the second mass is also removed in an external intermediate exchanger. Heat from the third and fourth beds is removed in the external cold heat exchanger and SO_3 gas cooler. As indicated above, the SO_3 gas leaving the converter is cooled in the tube side of the cold heat exchanger and SO_3 cooler by preheating the SO_2 gas leaving the blower and by forced air respectively.

An indirect air cooler reduces the SO_3 temperature to 300-350°F before going to the 98% sulfuric acid recirculating over the tower. The heat rise in the acid resulting from (a) the transfer of 93% acid, (b) heat of absorption of SO_3, and (c) from the sensible heat in the incoming gas, is removed from the acid as it flows by gravity through the 98% acid cooling heat exchangers to the pump tank. The exchangers are designed to reduce the acid temperature to 150°F. A vertical submerged pump recirculates the 98% acid over the absorption tower and also delivers the product 98-99% acid to the acid storage coolers or to the 93% acid system for dilution.

For heating up the converter system, valved ductwork is provided from the blower discharge to a heat source, either a separate gas fired heater or from some other source in the plant.

The double contact acid plant is the same as a single contact with the exception that the partially stripped gases at a higher SO_2 to SO_3 ratio are again passed through a portion of the converter and a second absorption tower. With this approach a 500 ppm acid plant emission can be guaranteed compared to 2000 ppm for a single contact. Figure 9 shows a single and double contact sulfuric acid plant schematic.

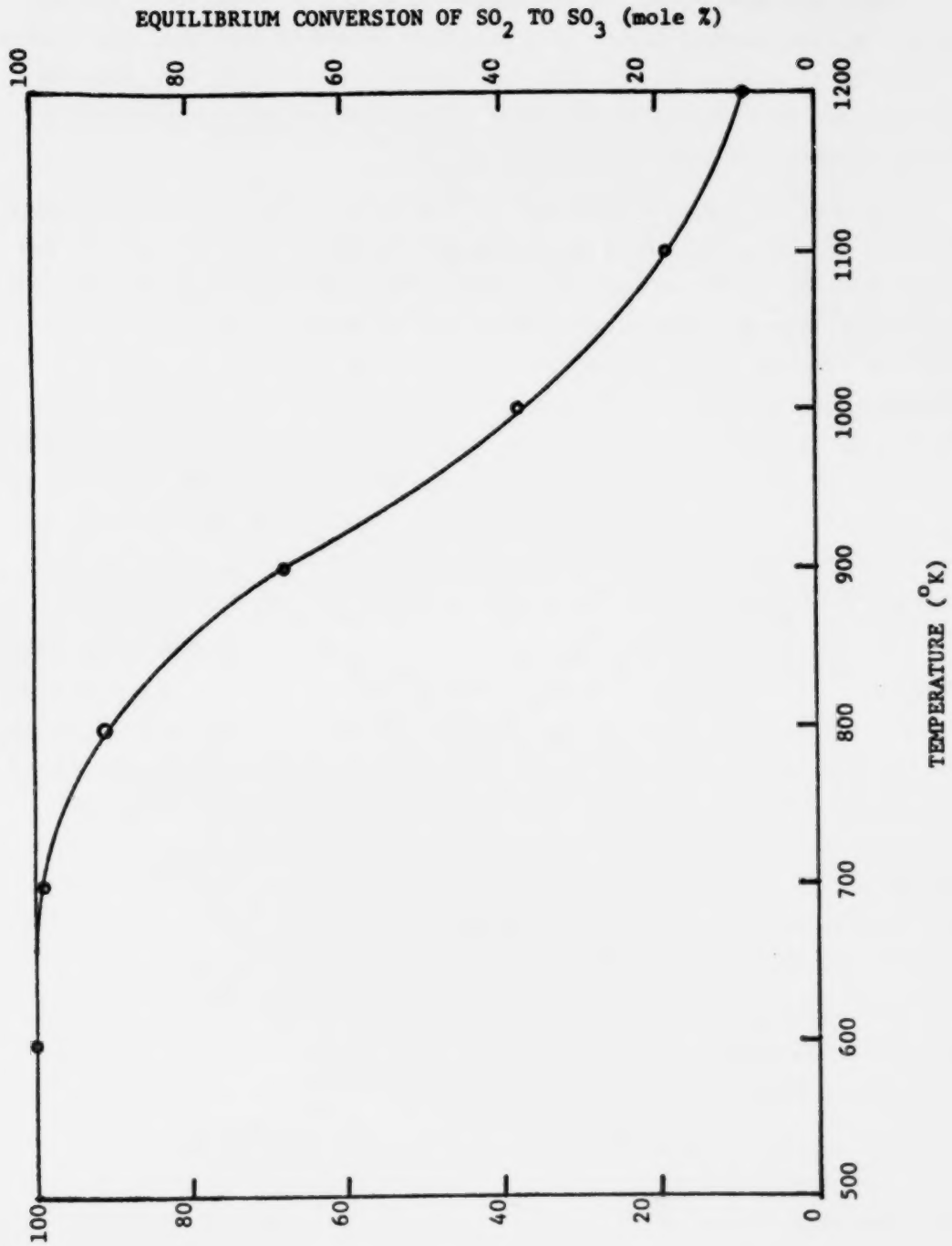


FIGURE 8. EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONVERSION OF SULFUR DIOXIDE TO SULFUR TRIOXIDE.
(INITIAL SULFUR DIOXIDE CONCENTRATION 8.0% BY VOLUME)

(Reference 11)

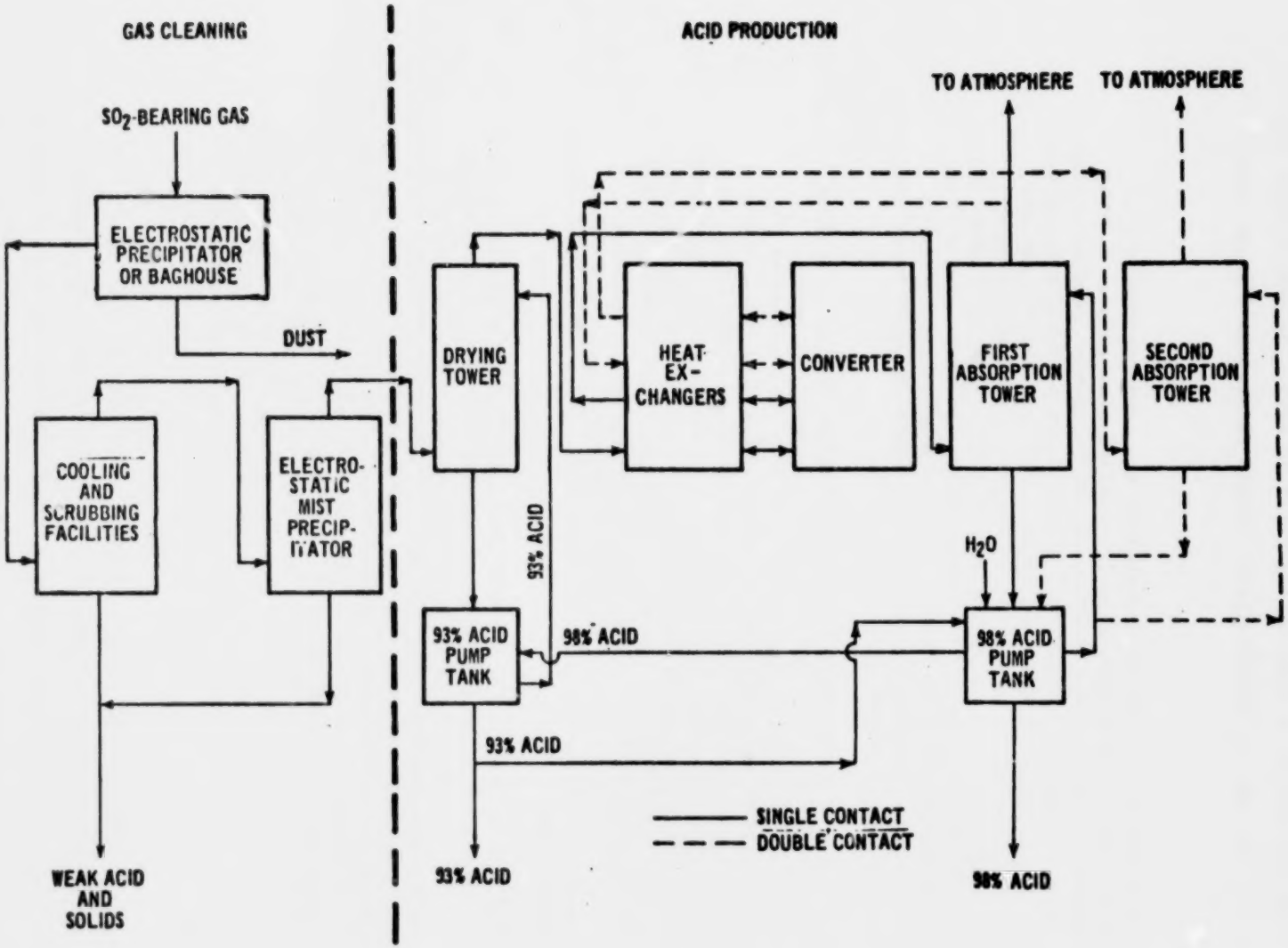


Figure 9: SINGLE AND DOUBLE CONTACT SULFURIC ACID PLANT SCHEMATIC

Reference 2

A clear discussion on some of the relative merits between single and double contact systems for metallurgical plants is presented below from Reference 10.

> "High sulfur dioxide concentrations are advantageous because they produce more acid for a given size plant. However, oxygen concentrations decrease as sulfur dioxide concentrations increase, and the oxygen concentration has a significant effect on catalyst performance and yield. For this reason, optimum sulfur dioxide concentration in a conventional metallurgical type contact plant is approximately 7.0 to 7.5% by volume. In the double contact or "interpass absorption" type plants first developed by Bayer in Germany, the optimum concentration is approximately 9.0% SO_2. However, equipment must be added to handle this stronger gas.
>
> As sulfur dioxide concentration decreases, smaller fractions of the reaction heat are available to preheat incoming cold gases. At approximately 3.5 to 4.0% SO_2 the acid plant is thermally balanced and any lower concentrations require the addition of external heat. The preheater provided for plant start-up can be used for this purpose but its continuous operation adds extra maintenance and fuel costs to the cost of acid production. It should also be noted that heat exchanger sizes increase rapidly as sulfur dioxide concentration decreases. With the double contact process, thermal balance occurs at approximately 6.0 to 7.0% SO_2 with 7.5% preferred as a practical lower limit.
>
> The conventional acid plant is considered to be a single contact (single absorption or single catalysis) process. This usually results in three passes of the gas through the converter with interstage cooling. Vendors will not guarantee any less output from the sulfuric acid plant than 2000 ppm with this system. For vendors to guarantee operation with SO_2 emissions at 500 ppm it is necessary to go to the so called double contact (double absorption or double catalysis) process where the main stream is brought out of the converter loop and a major portion of the SO_3 is removed from the gas in an intermediate absorption tower after two or three pass conversion. The balance of the gas is returned to the converter for a final one or two stages of conversion taking advantage of the kinetics to drive the SO_2 to SO_3 with a low initial concentration of SO_3."

The difference between single contact and double contact plants as far as additional equipment is concerned includes the absorption tower, additional heat exchangers and coolers as well as pumps, valves and dampers. While there is more equipment in a double contact plant, considering the kind of equipment plus the possibility of designing redundency in to the system, properly designed plants whether single or double contact should not exhibit a difference in reliability. A properly designed plant is one that is specifically

designed for potential problems and does have backup equipment such as spare pumps and valves and dampers etc. In many cases it is possible with proper circuitry to arrange a system that will allow by-passing of specific pieces of equipment so that the entire plant does not have to be shut down while this equipment is replaced or repaired. Designing for recognized problems that are known to occur will add to the initial capital cost of the plant but will save in terms of total maintenance cost over the life of the plant. The reliability of an absorption tower, where there are no moving parts, is going to be extremely high. Reliability of rotating or moving machinery is going to tend to be lower and because of this, design factors can be incorporated to compensate. Therefore even though there is additional equipment present, there should not be a major difference in the on time between single and double contact all other things being equal particularly if the system were designed to allow redundency and minimum maintenance.

4. Operating Problems

Corrosion control in an acid plant requires a major maintenance effort. Operation of the unit to minimize water formation in the SO_2 converter as a result of the flotation reagent carbon to CO_2 reaction must be made to minimize weak acid or so called "drip acid". If fluorine is present in the concentrate it must be removed by suitable scrubbing. The flourine will react with the vanadium pentoxide catalyst carrier. Materials of construction such as stainless steel, fiberglass, plastic lined glass, graphite or nickel alloys must be considered to minimize corrosion in the gas purification system.

Acid mist must be controlled from the acid plant particularly in the system adjacent to the drying tower. Sulfuric acid mist which may contain particles usually less than 5 microns is very difficult to remove from a gas stream. Electrostatic mist precipitators are normally used upstream of the drying tower to reduce the drying requirements. These are made of a series of 10 inch diameter lead tubes with hi-voltage discharge electrodes suspended in the center.

Usually a mist eliminator which consists of essentially a labyrinth of surfaces to catch and coalesce any small droplets is used downstream of the drying tower. The most successful appears to be one that is a

separate unit rather than part of the drying tower.

The temperature rise of the gas in a converter bed will, for example, be 285°F when using 8% SO_2 gas with approximately 65% conversion of the SO_2. With 4% SO_2 gas and 85% conversion, a temperature rise of 180°F can be encountered. At some minimum percentage SO_2 usually in the 3-4% range, the heat generated in the converter is not sufficient to maintain its optimum conversion temperature of 800°F. At this point it is necessary to either add heat in the converter or increase the concentration of the SO_2 stream. To accomplish both of these it may be desirable to use a sulfur burner as an auxiliary system for an acid plant attached to a smelter. When burning sulfur it is possible to generate whatever additional SO_2 is required, along with sufficient heat to allow a minimization of the SO_2 concentration.

Figure 7 shows a problem encountered in designing an acid plant when the SO_2 concentration is lowered. The gas temperature must be reduced to saturation temperature in the range of 68-80°F to provide the reduction in water content (water balance) necessary for continuously producing 93-98% H_2SO_4. As the SO_2 concentration increases to say 8% this temperature range may be from 97-110°F. Thus, the cooling capability of the system, which is dependent upon the water temperature available, is a critical factor. In some cases refrigeration or some additional technique may be required to produce acid from a lower concentration of SO_2. Thus, the economic balance of the concentration technique (which will, of course, add an additional system and its associated cost) must balance against modification of the acid plant to use lean SO_2 streams.

In some cases where fluorine is present the initial gas conditioning step is spraying the gas with water to remove this material. This step also reduces the temperature.

5. Effectiveness of Acid Plant For SO_2 Control On Copper Smelters

It has generally been found that the unique problems of smelters and smelter operations do not produce gas streams suitable for optimum sulfuric acid plant operation. Factors such as smelter repeated start-up and shut down, particulate cleaning, temperature control, and SO_2 stream low level concentration and the variability of this concentration all introduce difficulties for the matching of a sulfuric acid plant with a smelter.

A new single contact sulfuric acid plant will be guaranteed by the vendor to produce no more than 2000 ppm of SO_2 emissions. This includes all

acid or SO_3 converted and assumed to be SO_2 at the inlet. A double contact sulfuric acid plant is guaranteed by the vendor to produce no more than 500 ppm SO_2 on the same basis. These values are only guaranteed during the acceptance test period. However, in many cases it has been shown that with proper design these values can be reduced considerably. During the normal yearly maintenance time cycle for the catalyst, the performance of the plant will tend to deteriorate and therefore, the emissions will increase. Reference 2 indicates an emissions increase of as high as 30% can occur.

As long as the plant is on stream, the emissions will be controlled to the extent of its operating efficiency. However, because of the many every day problems that are encountered with conventional sulfuric acid plants and the additional problems encountered with the application of these plants to the smelter offgases, there is a significant time when the acid plant is not operating.

For example, the 9 year old plant at Phelps Dodge/Morenci (600 TPD) averages 21 hours per day of operation. When the plant is down the smelter can either shut down its operations (converter line or roasters) or will continue to operate and emit the full amount of generated SO_2, uncontrolled.

The major reason for the high number of acid plant shut downs is because the feed gas is interrupted or changed in composition as the operation of the smelter varies. This variation in smelter operation is a normal condition that will always be encountered as long as the present "conventional" equipment is being used. The acid plant is primarily a steady state device and therefore, is affected by startup and shut down variations related to efficiency and corrosion effects which will at the very least require an increase in maintenance efforts. Operation of the smelter can be modified within limits, to minimize these effects (e.g. programming converters) but they will always be encountered.

There are several approaches that can be taken to, in effect, make the acid plant "think" that it is operating continuously. These approaches and considerations are listed below:

- Provide a "preheater" to maintain heat when the SO_2 stream concentration is reduced below the autothermal condition.
- Provide an additional source of SO_2 to keep the acid plant operating when the smelter is down.

- Provide refrigeration equipment to reduce the gas cooling temperature to the range of 40 to 80°F.

A preheater and heat exchanger can be installed to increase the heating capacity to allow operation at below autothermal SO_2 stream concentration and will include the following:

Heat Exchanger
Direct Fired Air Heater
Controls and Safety Devices
Duct Work
Expansion Joint
Stack

An SO_2 generator can be installed to burn sulfur to generate sufficient SO_2 to maintain the acid plant in operation when the smelter is shut down. Start-up and shut down of sulfur burners can be a problem for this application although new designs appear to minimize this effect. Liquid SO_2 from a concentration system can also provide a source for acid plant feed gas adjustment.

A refrigeration system which would reduce the feed gas temperature to a point at which sufficient moisture would condense out (saturation conditions) to maintain the overall system water balance allowing concentrated acid production can be provided at the altitudes and locations of the Arizona smelters.

C. SO_2 CONCENTRATION SYSTEMS

Concentration systems are based on the ability of certain chemicals to absorb SO_2 at ambient temperature and the reduction in absorptivity at high temperatures allowing regeneration and recovery. Much development experience has been gained but the full scale application to an existing smelter must still be demonstrated on a long term basis. Brief mention of several typical systems follows:

1. Sodium Sulfite Scrubbing System

The Wellman-Lord SO_2 Recovery Process is now recognized as being operationally proven and ready for widespread commercial application. This process is a cyclic-regeneration offgas desulfurization process utilizing

a sodium sulfite-bisulfite solution as the sulfur dioxide absorbing medium. Concentrated sulfur dioxide is recovered as a valuable product and the sodium sulfite-bisulfite absorbent is thermally regenerated and recycled through the system. The process is essentially used for producing a concentrated sulfur dioxide gas from lean offgas streams.

After cleaning, SO_2 containing gas enters a tower where it counter currently contacts the absorbing solution of concentrated sodium sulfite which eliminates more than 90% of the sulfur dioxide in it according to

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2\,Na\,HSO_3$$

The sodium bisulfite is heated to drive off the SO_2 and reform the sodium sulfite. The sodium sulfite is concentrated and crystallized and centrifugally separated from the mother liquor, dissolved in the condensate from the cooler and recycled as absorbent. The SO_2 is generated at 98%.

The Wellman-Lord SO_2 recovery process has been applied to power plants, sulfuric acid plants, and petroleum refineries. The offgas volumes ranged from 40,000 to 124,000 SCFM, SO_2 concentration in pretreated offgas ranged from .21%to 1.3%, and the outlet gases contained 200 to 500 ppm (.02%to .05%) of SO_2. There are no known commercial sodium sulfite-bisulfite scrubbing systems installed to minimize sulfur dioxide emissions from either domestic or foreign primary copper smelters. However, a series of pilot plant tests were run on the smelter processes such as convertors and reverberatory furnaces by the vendor of this process, Davy Powergas Inc.

2. Magnesium Oxide (MgO) Scrubbing System

In this process a suspension of magnesium oxide is the absorbing medium. Sulfur dioxide in the offgases reacts with magnesium oxide to form magnesium bisulfite which is neutralized with magnesium oxide to form the sulfite. Magnesium sulfite is then calcined to yield sulfur dioxide and magnesium sulfate is also formed and has to be removed.

There is no known installation of this system in the U.S., but a commercial magnesium oxide-base absorption system was developed and applied to the Onahama Smelter in Japan. These outgoing gases were rich in SO_2 (13-15%) and were used to manufacture sulfuric acid.

3. Dimethylaniline (DMA) and Xylidine Scrubbing Systems

DMA absorption was developed by the American Smelting and Refining Company (ASARCO). The system is a cyclic-regenerative process. Liquid sulfur dioxide is recovered as a product, and the absorbent is regenerated and recycled through the system. A small amount of sodium sulfate formed in the regenerator is removed by using a small purge stream.

DMA process has been used in the United States to recover sulfur dioxide from smelter gases containing 4 to 10 percent sulfur dioxide. The process has been applied to lead sintering machines offgases (ASARCO Selby smelter) and to blended effluents from copper smelter roasters, reverberatory furnaces and convertors. (Tennessee Copper Company Copperhill Smelter). A new DMA system designed to recover SO_2 from the Phelps Dodge/Ajo copper smelter has operated with SO_2 concentration in offgases ranging from 1.5 to 2%. It should be noted that PD has encountered great difficulty in operating this plant since its installation. Design deficiencies became apparent soon after start-up and a succession of mechanical failures has prevented the plant from operating to any great extent. None of the problems, however, appear to be fundamental to the successful application of this system. A value of SO_2 concentration in offgases below 1.5% can lead to unfavorable equilibrium between DMA and SO_2 resulting in uneconomical recovery of SO_2.

The Lurgi Sulphidine process utilizes and aqueous xylidine scrubbing media and is primarily applicable to lower SO_2 concentrations in inlet streams than is DMA. This system was used in Europe by Metallgesellschaft.

4. Ammonia Absorption System (Cominco Process)

The ammonia absorption process was developed by the Consolidated Mining and Smelting Company of Canada Ltd. (Cominco). Plant units have been built at Trail, B.C., Canada (offgases from lead and zinc smelter) and in Texas (tail gases from primary sulfuric acid plants).

The Cominco process employs a solution of ammonia as the absorbent. The process has been employed on a large scale for more than 30 years for treatment of dilute gases (about 1% sulfur dioxide) from lead ore sintering machines. The gases are cleaned and conditioned before entering the absorber. The process can be used for treatment of gases from copper reverberatory furnaces, although it has not actually been so employed. Processes similar to Cominco process have been commercially applied to pulp and paper industry.

The spent absorbent is regenerated by acidifying with sulfuric acid to release concentrated sulfur dioxide and to form ammonium sulfate as a by-product. The economics of the process are strongly dependent upon the existance of adequate markets for the ammonium sulfate produced.

The Cominco process seems to be a promising method that can be applied to control SO_2 emissions from precleaned and conditioned smelter process offgases that have SO_2 concentrations in the range of 0.5 to 6.0 percent. The economics of ammonium sulfate and ammonia may inhibit the use of this process for the Arizona smelters.

D. REDUCTION OF SULFUR DIOXIDE TO FORM ELEMENTAL SULFUR

Elemental sulfur plants have never achieved widespread use within the non-ferrous smelter industry. This is because of the fact that the favored method of control of smelter gases continues to be manufacture of sulfuric acid by the contact process. The additional requirement of a reducing agent, which invariably is a fuel such as gas or coal, will inhibit the use of this process as long as the energy problem is present.

The Allied Chemical Corporation reduction process has been applied commercially and on a large scale to pyrrhotite roaster gases containing about 12% sulfur dioxide. An increase in SO_2 concentration in offgases makes the process more economical. For dilute gases, a preliminary concentration step (e.g., Wellman-Lord, DMA etc.) is required.

Three companies are involved in actively developing SO_2 reduction technology. The Allied Chemical process uses natural gas as the reducing agent, which is undesirable in the face of the diminishing supplies and increasing costs of natural gas. However, the process can be operated on a producer gas generated from coal. The Outokumpu technology developed in Finland is restricted to flash smelting furnaces and uses oil or pulverized coal as the reducing agent. ASARCO/PD SO_2 reduction technology is still in the pilot plant stage of development. In this process, reformed natural gas is produced in a process developed by Phelps-Dodge. The process would require precleaning and purification of smelter offgases.

In each of the SO_2 reduction technologies, the reducing agent is the largest single element of operating cost associated with each process. Unlike the sulfuric acid by-product, elemental sulfur is a by-product that can

be stored indefinitely at low cost. Freight costs are relatively low and sulfur can be economically shipped for longer distances than sulfuric acid.

The Citrate Process for the recovery of elemental sulfur from SO_2 emissions in waste gases was conceived by Bureau of Mines investigators. In this process, the absorbent is the sodium salt of a stable, non-volatile weak acid (e.g., sodium citrate), which forms a basic solution by hydrolysis. The anion of the acid buffers the solution as acid is formed by the absorption of sulfur dioxide. The spent absorbent, which consists of a solution of sodium sulfite and bisulfite and of the weak acid, is contacted directly with hydrogen sulfide. The hydrogen sulfide reacts with the sulfite and bisulfite to yield elemental sulfur, and the regenerated basic salt solution is recirculated to the absorption step. One of the problems with the system is that some of the sulfur dioxide is oxidized to sulfate, which is not readily regenerated, and thiosulfate and polythionates are also formed. Consequently, it is necessary to draw off purge streams of the absorbents, recover the citrate for reuse, and discard the sulfate and thionates. Losses of citrate in this operation can have major effects on the economics of the processes.

The Citrate Process was tested on three units, (a) a 400 cfm pilot unit which began treating reverberatory furnace gas at a copper smelter in Arizona in November 1970, (b) pilot plant designed to treat 1000 cfm of 0.5% SO_2 gas, now constructed and operating at the Bunker Hill Lead Smelter, Kellogg, Idaho, and (c) a 2000 scfm unit operating on the coal-fired spreader stoker type boiler at a power plant in Terre Haute, Indiana since June, 1973. For case (a) a series of mechanical difficulties allowed only for intermittent operation of the demonstration unit and only a limited economic and engineering data on the process was generated. While the process chemistry seems sound the requirement for H_2S will limit its application to smelters.

E. OXYGEN ENRICHMENT

1. Chemistry

The chemistry of the smelting of copper requires considerable additions of oxygen since major steps in copper reduction are converting copper sulfides into copper oxides and iron sulfides into iron oxides. This requires the reaction of the sulfur with oxygen which primarily forms SO_2. See Appendix A. Since the reaction must be initiated at high temperature and also since high

temperatures are required to reduce feed materials to the molten state, a combustion reaction is also required to react with a fuel which can be either coal, oil or gas.

Past and most of the current practice has been to use air to supply the oxygen. Since air consists of approximately 21% oxygen and 79% nitrogen, a major portion of the fluid supplying the oxygen is inert and does not contribute to the process. In fact, since the nitrogen must also be heated it actually takes away heat from the smelting process, and should be considered as a detrimental or at least costly ingredient.

2. Smelting

Most copper smelters today are using oxygen (liquid supplied by trucks to special insulated storage tanks) to a limited extent. Oxygen mixed with the blowing air for converters is the principle application. This may be done usually when it is desired to increase production for a short period of time. Cost of trucking in oxygen tends to inhibit its use.

The advantage of using oxygen enrichment, from an SO_2 control standpoint, is that smelter off-gas stream concentration tends to increase, qualifying more gas for sulfuric acid plant feed. In addition, reduction of the amount of nitrogen in the gas reduces the total gas volume flowing which can then minimize gas system and acid plant equipment. Also, with reduced nitrogen, more heat is available for processing, reducing fuel consumption.

The most beneficial use of oxygen to facilitate SO_2 control would be in the reverberatory furnace. Here, SO_2 concentrations of 0.6% to 1.5% are encountered. None of the smelters in Arizona are currently collecting SO_2 from the reverberatory furnace. (Phelps Dodge/Ajo will be sending reverberatory furnace gases to a DMA concentration system). As long as the conventional reverberatory furnace is used, a gain in SO_2 collection from oxygen enrichment can be significant since the total quantity of SO_2 generated within the reverberatory furnace is in the 15% to 30% range of that emitted from the entire smelter.

Oxygen is used as part of some of the new basic processes such as the flash smelting systems. However, these processes inherently require its use to be commercially feasible and would not require regulatory encouragement once they have been installed. Most of the new processes result in

sufficiently rich SO_2 streams (even those not requiring oxygen such as electric furnace reduction) to allow direct feed of the offgas to an acid plant.

3. Oxygen Addition

a. In Reverberatory Furnace

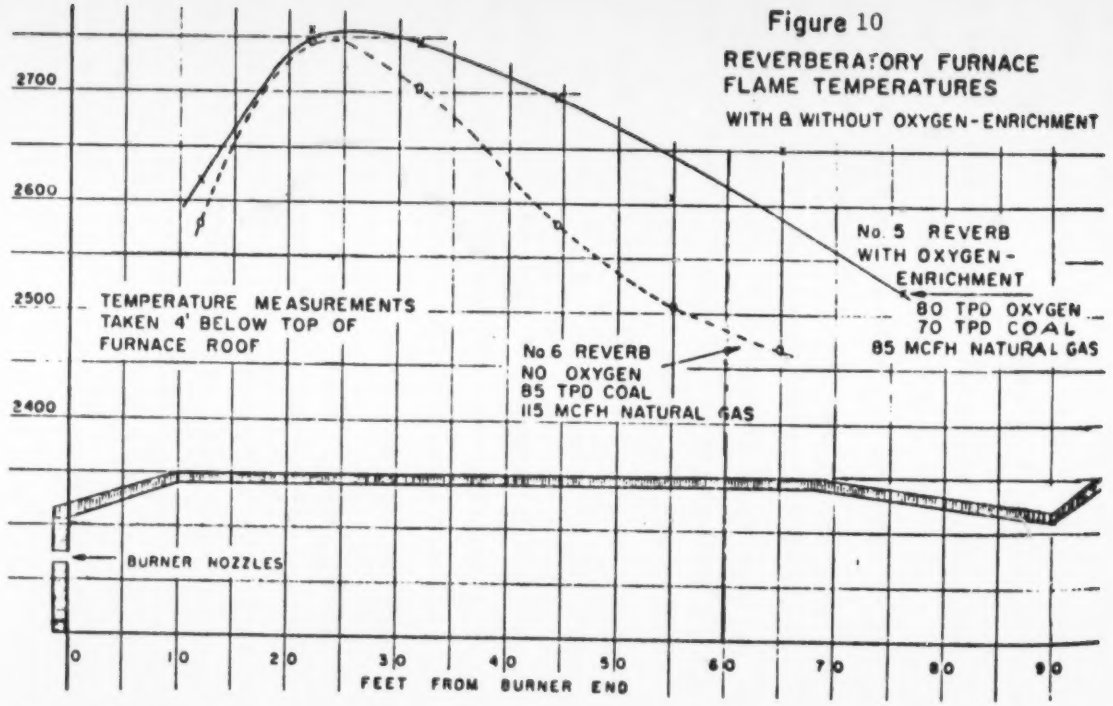
Oxygen addition to the air entering the reverberatory furnace can permit combustion of larger volumes of fuel thereby increasing smelting throughput. About 45% of the gross thermal input in an air/fuel fired reverberatory furnace leaves as sensible heat in the nitrogen. The amount of heat carried away by each ton of nitrogen is of the same magnitude as that required to smelt one ton of solid charge. Therefore, fuel efficiency can also be increased by increasing the percentage ratio of oxygen to nitrogen. It should be noted that in most cases a waste heat boiler is installed at the reverberatory furnace gas outlet to capture up to 50% of the heat leaving in the gases. The optimum amount of oxygen used if fuel efficiency were the only criteria must be adjusted accordingly. The iron sulfide compound in the feed concentrates tends to be preferentially oxidized at temperatures below 1500°F to magnetite (Fe_3O_4) rather than ferrous oxide (FeO). The objective in the smelting process is to react iron oxide with silica in the flux to form ferrous silica slag. Magnetite must be reduced to ferrous oxide by reacting with iron sulfide at temperatures above 2100°F.

The addition of oxygen can produce increased temperature in the reverberatory furnace raising the temperature of the slag. It has been found that higher temperature slag tends to reduce copper losses by as much as 15-23% because of the lower slag viscosity allowing faster settling of copper containing particles. This reduces the amount of small particle copper that is retained by the slag allowing more to enter the matte (Reference 3 and 4).

One of the major concerns in introducing oxygen and its resulting high temperature is the durability of the furnace refractory materials. It has been found that material temperatures increase by 0.5°F per MSCF oxygen added. It has also been found that the flue gas itself will increase in temperature about 1.2°F per MSCF. Data from studies on smelting of nickle in a reverberatory furnace with and without oxygen enrichment, shown in Figure 10 from Reference 5 indicate even less material temperature effects with oxygen. Temperature measurements were taken 4 feet below the top of the

Figure 10

REVERBERATORY FURNACE
FLAME TEMPERATURES
WITH & WITHOUT OXYGEN-ENRICHMENT



—JOURNAL OF METALS, APRIL 1966

Reference 5

furnace roof. At a length of 9 feet from the burner end there is a difference in the peak measured temperature of 2750°F. In the case of oxygen enrichment, the temperature did remain higher over this length once the peak had been reached. In other words, there was a more rapid drop in temperature without the oxygen enrichment. The amount of fuel was also reduced from 85 TPD of coal plus 115 MCFH natural gas to 70 TPD of coal and 95 MCFH of natural gas with an addition of 80 TPD of oxygen.

It appears from these numbers and based upon an oxygen cost of $17.00 per ton, (See Section E-4) that there is not an economic advantage to using oxygen just to reduce fuel consumption. Experience has also shown that it is undesirable to exceed the base flue gas rate by more than 5% in a reverberatory furnace to prevent exceeding the normal operating range of flue gas temperature. However, it has been noted (Reference 6) that an additional 3 to 8 tons of green charge can be smelted per ton of oxygen. Depending upon the special smelter cost distribution (i.e. labor requirements, labor rate, custom vs captive ore, copper price, etc.) the smelting rate can generally be increased and result in a net profit gain.

The nomograph Figure 11 from Reference 6 shows the relationship between natural gas rate, wet reverb smelting rate and tonnage oxygen required. Figure 12 from the same reference shows the same relationships along with the resulting SO_2 percent (dry) and flue gas (wet).

The curves were obtained from a mathematical model developed by Linde for a copper smelting reverberatory furnace and can serve as a guide to adjusting furnace operating parameters to obtain the most economical production consistent with maintaining a high enough concentration of SO_2 to produce satisfactory acid plant feed streams. Offgases containing 3.5%to 5% SO_2 have been obtained from reverberatory furnaces with oxygen addition. Therefore, net cost of adding oxygen must include credit for increased production as well as fuel savings.

Depending upon the furnace construction and whether a roaster or wet charge is used either oxygen enrichment of the primary combustion air or auxiliary oxygen roof burners can be used. In some cases it may be advantageous to use a combination of both. Actual numerical values of the operating parameters must be determined by test of each individual furnace.

The controlling factors in the application of oxygen are the furnace refractory and slag temperatures and the auxiliary material handling capa-

bilities. Roof temperature must not exceed the maximum of the allowable operating range. On the other hand the slag temperature should be as high as possible without becoming too difficult to handle. The higher the slag temperature, the less limestone need be added to the fluxing materials to promote good fluidity. In the operation of reverberatory furnaces on air-oxygen blast it was indicated (Reference 4 and 5) that wear on the furnace lining of the furnace arch with oxygen was the same as when conventional air blasts were used.

From Reference 4 it was noted that with a spring arch roof of 460 mm of chrome-magnesite bricks, wear in the highest temperature region was 62 mm after one year. During the period when 25% oxygen was used there was no difference in the roof wear. During a year long test program where oxygen enrichment was increased to 35% and fuel rates varied considerably, taking into account the measurement accuracy, the wear of the furnace roof during reverberatory furnace operation on oxygen enriched blast did not differ markedly from when operating with conventional air blast.

Analysis of the flue gases over the O_2 range in a series of tests indicated that 3.5 - 5.0% SO_2 concentration levels can be obtained (Reference 4). The reverberatory furnace gases were fed directly to an acid plant. Blending with converter or roaster gases is also possible.

During the various oxygen test programs, the limiting factors were the roof temperature and the material handling capacity. Generally, excessive roof temperatures did not become a problem until production increases of over 50% were attempted. Matte handling limitations became prevalent only when crane problems were encountered. Slag handling became difficult with excessive fluidity, i.e. temperature, but this was easily corrected by an adjustment in the silica content of the feed. Supplying sufficient feed to the furnace was generally no problem. Another limiting factor, if the production rate of the furnace is increased, is the reduction in settling time available for the copper containing materials added to the charge.

Another possible advantage to the use of oxygen was noted during a particular test applying oxygen to maximize production. During this program the increase smelt rate and matte temperature caused a washing effect to occur on the furnace bottom. As a result, the average furnace bottom was reduced by an average of 3" during a month's period.

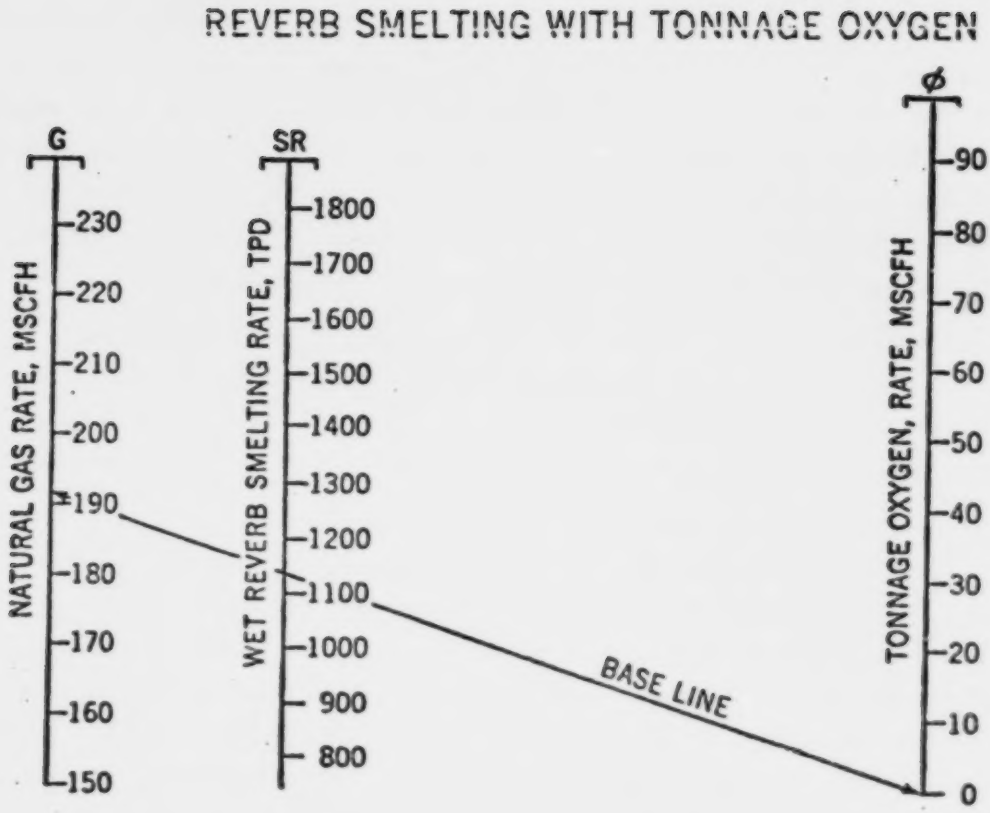


Figure 11 Reference 6

REVERB PRODUCTION AND FLUE GAS DEPENDENCE UPON TONNAGE OXYGEN AND FUEL

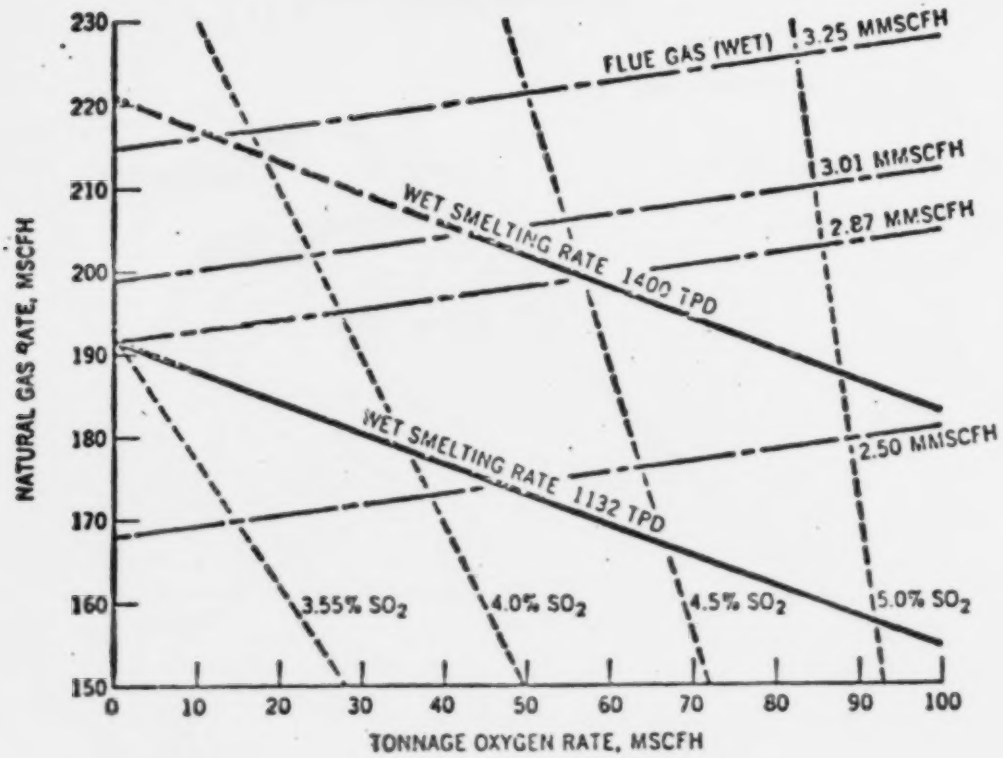


Figure 12 Reference 6

- REVERB SMELTING

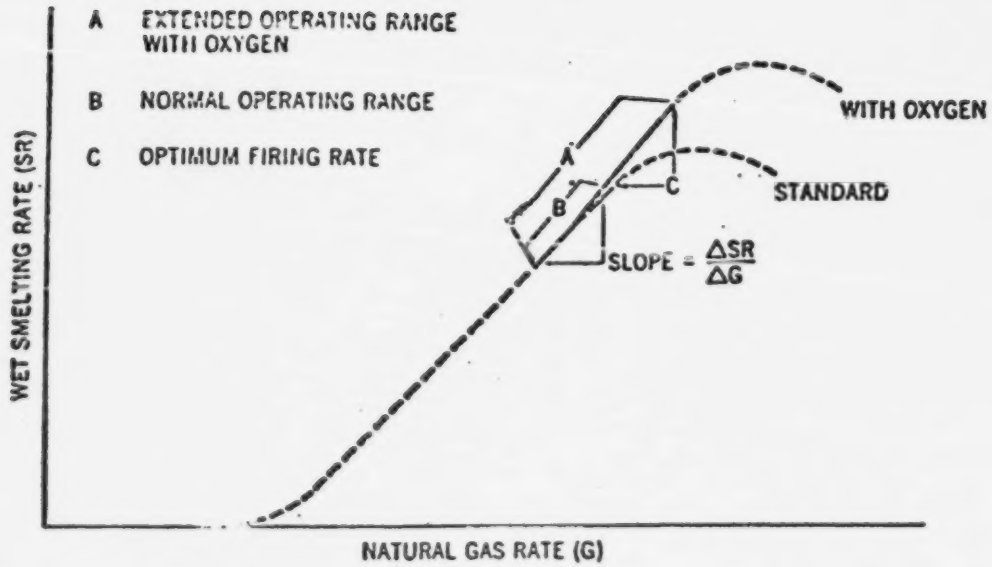


Figure 13 Reference 6

Oxygen was also used in an oxygen burner to clean out the furnace bottom by actual melting. It was found after a reduction of 2 feet in the furnace bottom, removing better than 10,000 cu. ft. of material, that an average oxygen consumption of 13 MSCF per ton of material removed was used.

The capability of increasing the production rate of the reverberatory furnace can be shown in the typical smelting curve in Figure 13. This shows wet smelting rate versus natural gas rate and indicates that a peak is encountered. It is normally desirable to operate (at maximum efficiency) just before the curve peaks. As noted, with the use of oxygen the peaking point occurs at a higher smelting rate.

With oxygen enrichment it will be necessary to minimize reverberatory furnace openings and introduce control systems to ensure that the internal pressure stays very slightly, but always, below atmospheric pressure. The reduction in flue gas flow can tend to reduce the pressure in the furnace which would then cause an increase in dilution air which could then reduce the advantage of the increased SO_2 content.

Green charge furnaces will tend to produce a higher SO_2 concentration but will also have a greater variation in concentration because of the possible variation in sulfur concentration of feed materials. Each smelter must investigate the effects of specific local conditions such as feed material and equipment to optimize the oxygen enrichment techniques. If SO_2 variation is significantly below the acid plant autothermal temperature, the preheater may be required. It should be noted, however, that thermal lag in the catalyst system will allow periods of at least 15 minutes with the input gas below autothermal temperatures. Furnace SO_2 variances, reflecting charge times, tend to fall within this cycle range.

b. Converters

The reaction of the magnetite with iron sulfide is shown in the following equation:

$$3\ Fe_3O_4 + FeS \longrightarrow 10\ FeO + SO_2$$

In the converter the iron sulfide can also be oxidized to iron oxide as

$$FeS + 1.5\ O_2 \longrightarrow FeO + SO_2$$

and also

$$3\ FeS + 5\ O_2 \longrightarrow Fe_3O_4 + 3\ SO_2$$

$FeO + Fe_3O_4 + SiO_2 \longrightarrow$ Iron silicate slag containing magnetite. The higher the operating temperature the less the reaction favors magnetite.

While the material that enters the smelter such as concentrate, reverts and scrap can vary, lower concentrate grade can by-pass the reverberatory furnace and be fed directly as green feed to the converters if oxygen enrichment is used. This is possible because of the additional heat generated with the oxygen.

In those cases where production increases may be desired (high ore availability) oxygen addition can increase converting rate.

Combining 80 tons of concentrate, after matte in the converter has formed a molten base, for example, then skimming, then adding 40 more tons of this concentrate followed by routine cycles of slag blowing, skimming and matte addition has been done on a routine basis with oxygen addition.

The use of oxygen enrichment, while not necessarily improving the SO_2 concentration out of the converter, can provide an additional dimension in the operation of the smelting system and also greater flexibility with variation in the feed. This should be particularly useful for custom smelters.

The results of experiments Reference 8 showed the output of a converter increases proportionally to the increase in the oxygen content of the blast. With 35% oxygen it was also noted that systematic cleaning of the tuyeres was no longer necessary. Blast losses caused by this operation are therefore reduced. Reduced ferrite formation is also noted. The sulfur dioxide content in the converter gases increased proportionally with an increase in the oxygen content. As a result of the reduction in the volume of the gases and the volatilization action of a large amount of the accompanying metals the dust content in the gases increased. It was found possible to process a larger amount of cold additions because of the higher energy that is available for the converting process. The limiting factor with regards to the intensification of the converting process was durability of the refractory brick in the converter.

c. Roasters

With the fluidized bed roaster there does not appear to be a major advantage in using oxygen enrichment. With the gas flow required for fluidi-

zation, SO_2 concentration from roasters is sufficiently high to use directly for acid plant feed.

In the case of multi-hearth roasters, oxygen enrichment may in some cases be an advantage but would probably be somewhat questionable because of the large losses and air dilution that tends to result with these units in the Arizona smelters.

4. Oxygen Cost and Availability

The lowest cost approach to providing on site tonnage oxygen is to allow the oxygen vendors to build and operate a plant either adjacent to or on the smelter grounds. Under these circumstances present day costs are estimated to be as follows:

Plant Size Tons per Day	Oxygen Price Dollars per Ton
50	25
100	23
400	19-20
700	15-17

This assumes that a contract will be agreed to between the smelter and the oxygen vendor for a period of 15 years. A 10 year agreement will increase oxygen cost.

These numbers also assume electrical power is available and will cost about 12 mils per K.W.H. The curve in Figure 14 from Reference 9 shows the power requirements versus daily production rate. Power is the major direct operating cost for producing tonnage oxygen. It represents approximately 65% of the total direct operating costs.

The basic process for large tonnage oxygen is usually a modification of the Joule-Thompson method where air is liquidified and the oxygen then differentially distilled. For very small quantities, the oxygen can be trucked in and stored in insulated tanks, however, for the smelters in Arizona this is not an economical approach when large tonnages are used.

The location of an oxygen plant near the smelter would also allow more economic use in the smelter converters and adjustment of SO_2/O_2 ratio in the acid plant for efficient conversion without dilution.

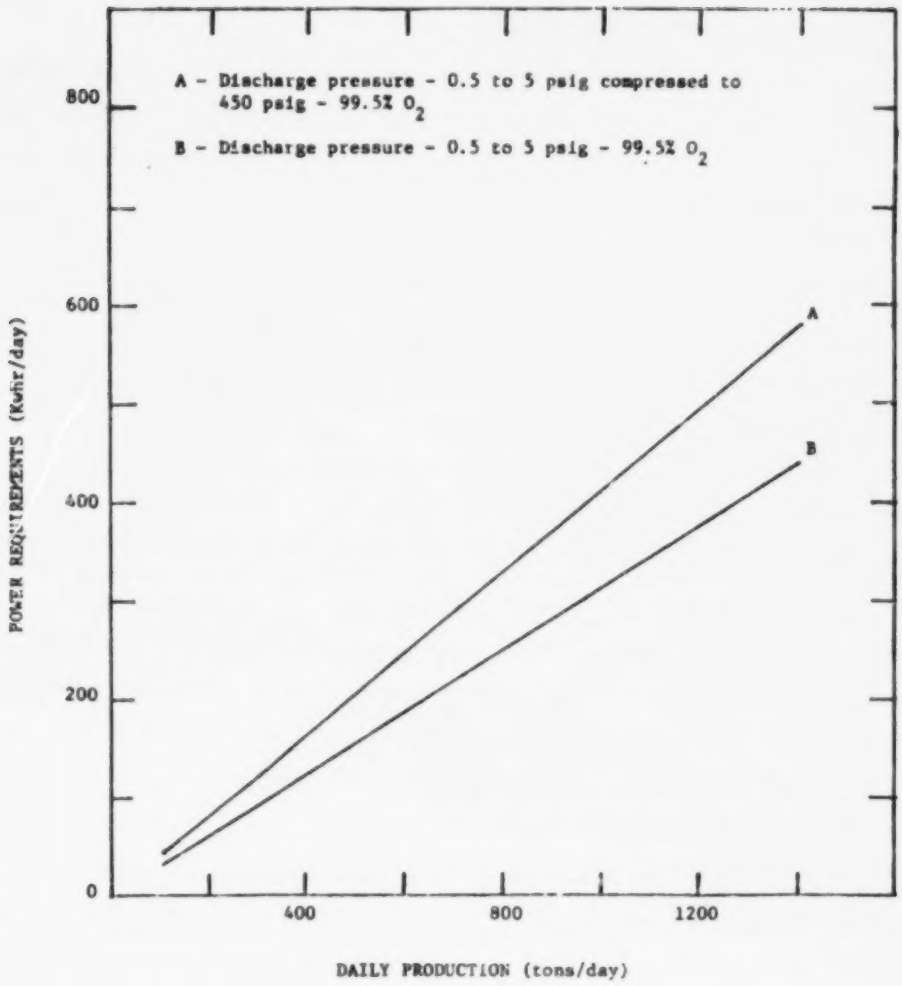


FIGURE 14. POWER REQUIREMENTS FOR TONNAGE OXYGEN PLANTS. DAILY PRODUCTION VS. POWER REQUIREMENTS. (Reference 9)

F. SCRUBBER SYSTEMS RESULTING IN WASTE PRODUCTS

The wet lime (lime slurry) process has most favorable application where small quantities of dilute (0.6-1.5% sulfur dioxide) gases have to be treated to solve air pollution problems. The process is less suitable for situations where there are large volumes of offgases, (high capital and operating costs) or where the concentration of sulfur oxides is high (large quantities of throwaway product). The wet limestone (limestone slurry) process has application similar to the wet lime process, except that it is less efficient at removing sulfur oxides from the gases and has somewhat lower capital and operating costs.

As noted in Reference 2, there are no known applications of lime and limestone scrubbing systems installed to control sulfur dioxide emissions from either domestic or foreign primary copper, lead or zinc smelters. The reasons for this are presumed to be economics since a throwaway product ($Ca\ SO_3 + Ca\ SO_4$) is obtained from the scrubbing system. Calcium based scrubbing systems have been applied to control SO_2 emissions from fossil-fuel-fired power plants, as well as a secondary lead smelter, a molybdenum ore roaster and an iron ore sintering plant. The SO_2 concentrations in the process offgases from the above processes were less than 6000 ppm (0.6 percent).

The two systems (lime slurry and limestone slurry) are essentially the same except that in the lime slurry system, limestone is calcined to calcium oxide prior to introduction into the scrubber slurry feed system. A major problem with the limestone process is that limestone is not as reactive as lime, and therefore, large quantities of limestone is required along with a larger scrubber with higher slurry recirculation rates, hence making limestone systems less efficient than lime systems as already noted.

Scrubber design, liquid to gas flow, pH value of slurry, inlet gas temperature, type of limestone and its particulate size, and slurry solids loading are the various scrubber parameters which influence the SO_2 removal efficiency and operation of limestone scrubbing systems. A major operating problem with both calcium based scrubbing systems arises in the scrubber and associated lime slurry facilities. The various solid constituents; namely lime, limestone, calcium sulfite, and calcium sulfate have strong scaling tendencies. Severe plugging of lines and equipment could occur due to the hard deposits that build up on surfaces exposed to the liquid. Another obvious problem is the conditioning and handling of throw-away wastes

($Ca\ SO_3 + Ca\ SO_4$).

G. LIQUID SO_2/ACID PLANT

Whenever a concentrated stream (80%-100%) of SO_2 is available, it can be compressed to a liquid and stored indefinitely at ambient temperature. With a supply of liquid SO_2 available to the smelter operation of acid plants can be considerably improved by adjusting feed gas concentration to the optimum. This will eliminate the effect of smelter equipment operating variability.

H. CONCLUSION

The current most readily acceptable and available SO_2 control technique for primary copper smelters is the conversion to sulfuric acid in a contact plant. Experience with this technique in smelters has been obtained over nearly 50 years and has proven satisfactory.

The major economic problem in using sulfuric acid technology as the collection medium for SO_2 is the selling or distribution of the product. The price of sulfuric acid varies with economic conditions. In 1974 the demand was so great that acid could be sold at relatively great distances (over 300 miles) from the source. The cost of shipping acid, which requires special tank cars or trucks, is sufficient to eliminate the long haul customer. Thus, if the acid market or price of acid reduces it becomes unprofitable to sell. The cost of neutralizing the acid versus shipping to a customer in an unprofitable situation must then be evaluated.

Storage of sulfuric acid is limited because of the costly tankage required. The storage of elemental sulfur is considerably easier since it can be stored outside and unprotected except perhaps for severe wind conditions. If it is watered down it can cake and thereby become a stabilized mass. It can be handled with ordinary earth moving equipment and therefore can be shipped at much lower cost. As mentioned previously the requirement for a reducing agent (fuel) will raise the cost of producing the elemental sulfur. Also the availability of the fuel may in the future be limited because of the energy situation.

With the shipping and fuel problems present with sulfuric acid and elemental sulfur it then becomes necessary to also evaluate concentration systems to provide liquid or gaseous SO_2 as a product or for gas stream con-

centration adjustment to improve acid plant operation.

All of the remaining methods for SO_2 collection fall in the category of "potentially available". In all cases these involve either the production of sulfuric acid, elemental sulfur, liquid SO_2 or neutralization.

A further factor that must be considered is other uses for either the sulfur or sulfuric acid within the smelter area. These other uses could include leaching, fertilizer production, or production or other chemicals that use sulfuric acid or sulfur as an intermediate.

The economic picture is a complicated one that is continuously changing and since it takes in the order of three years to install new process equipment the decision to take a certain path for SO_2 control is a difficult one.

It should also be noted that in the discussion in this report we have limited ourselves primarily to retrofit equipment. There are processing techniques that can be introduced to at least minimize or reduce SO_2 emissions. These techniques can, for example, include elimination of more SO_2 in the roasters before entering the reverberatory furnace to reduce furnace emissions or programming of converters to provide a more constant SO_2 stream quantity and concentration. Process changes therefore should be considered along with positive control techniques.

In all cases the local conditions at each specific smelter will control the decision as to the choice of positive control techniques.

V. REVIEW OF POSSIBLE SO_2 CONTROL APPROACHES FOR EACH SMELTER

A. INTRODUCTION

The techniques for SO_2 control from copper smelters discussed in the previous sections of this report have been applied to the individual smelters considered in the State of Arizona. The primary "available" technique used for this study is the application of a sulfuric acid plant to collect SO_2 in stream concentrations of 4.0% by volume or greater.

The remaining techniques considered are believed to be potentially available. This definition has been applied and processes selected only if they have been developed through research, pilot plant, and have been operated at full plant scale. The reason for considering them potentially available is that they have not had "sufficient" every day experience in a full producing smelter application. "Sufficient" must be judged by problems encountered and solutions that have or may be employed.

The purpose of including potentially available techniques is to indicate that the technology exists to collect even the lean SO_2 streams such as emitted from reverberatory furnaces or multihearth roasters and to provide a relative measurement (time and cost) for evaluating their applicability to each individual smelter.

B. ASSUMPTIONS AND GROUND RULES FOR PREPARING ALTERNATIVE CONTROL TECHNIQUES

1. Capital costs and procurement time schedules are intended to be order of magnitude and are not a result of detailed engineering analysis and design studies taking into account specific and unique installation problems that can be expected for each smelter.

2. Costs were based on current time.

3. It is necessary to separate costs for smelting equipment from costs of pollution control equipment to establish true control costs. Where process equipment must be installed to replace obsolete or not repairable equipment, its cost is not a legitimate pollution control cost since the equipment is used to produce copper. It is recognized that in some cases the smelter could "get by" without replacing old equipment if pollution control regulations could be ignored, but the equipment would in all cases eventually have to be replaced. The new equipment is needed for production and in practically all cases improves the process efficiency thereby reducing costs to produce the product. It should therefore be considered as part of the process costs rather than the pollu-

tion control costs.

For purpose of this study, only equipment that does not directly take part in copper production was considered for classification as pollution control equipment.

4. Relatively little consideration has been given to the use of so called "scrubber" systems wherein the SO_2 is neutralized with lime or its derivatives. The main reasons for this are discussed in Section IV-A-2 and include questions on the effects of gas stream impurities, availability of water and characteristics and disposal economics of waste products.

5. Systems that result in the production of sulfur could be considered as producing a useful product. However, the requirement for the reducing agent which introduces cost and availability questions because of the current energy problem will tend to inhibit the use of this process. The sulfuric acid/sulfur market/storage question must be considered for each individual smelter and will vary with time. It therefore, was considered to be somewhat beyond the scope of this report although production of sulfur can be considered as a potential viable alternative.

6. The techniques considered were based upon the capability of being retrofited to the existing Arizona smelter equipment. It should be noted here that additional process changes using equipment with no alteration can have in many cases a marked effect upon the ability to control SO_2 emissions. For example, programming converter operation to reduce the major fluctuations that can occur in the gas emissions from a smelter line can materially improve the operation of a sulfuric acid plant and avoid many maintenance problems. These process type changes were not included as part of the alternative listings in this section even though it is considered that they are very definitely potential alternatives to positive control.

7. Weak stream control costs from either reverberatory furnaces or multihearth roasters can be minimized by closing off leaks in equipment to eliminate extraneous dilution air.

8. There was no adjustment in the cost for revenues generated by pollution control system product sales or additional cost due to neutralization of sulfuric acid as a result of market conditions. These two factors have a tendency to balance each other over long periods of time depending on market fluctuations.

9. If an acid plant (single contact) input gas stream is less than 4.0% SO_2 (by volume), additional preheating capacity is required. It is assumed that an additional 15% of the original capital cost of the plant will be required to purchase and install the preheating equipment which includes direct fired heater, heat exchanger, controls and safety devices, ductwork, expansion joints and stack. Base operating cost for fuel usage for the preheater is calculated for a plant with 85,000 SCFM flow as $433,000 per year to heat ambient air to 800°F. Operating cost

is assumed directly proportional to flow and will increase as percent SO_2 decreases according to the usage factor related to average % SO_2 shown below.

$$\frac{\text{SCFM}}{85{,}000} \times \$433{,}000 \times \text{Usage factor} = \text{operating cost/year}$$

Average % SO_2	Usage Factor
3.35	.40
2.60	.80
1.90	1.00

10. If an acid plant input gas stream is less than or equal to 1.5% SO_2 (by volume), refrigeration equipment is required along with the preheater to insure sufficient gas dehumidification to maintain system water balance. An additional 15% increase in the capital cost of the plant for refrigeration will be required. Base operating cost for energy usage for the refrigeration system averages $18.00/hour over a one year period for a 900 TPD acid plant operating in the 1.0% to 1.5% SO_2 range. A linear relationship with acid plant size was assumed as

$$\frac{\text{TPD}}{900} \times \$18 \times 350 \frac{\text{day}}{\text{yr}} \times \frac{24 \text{ Hr}}{\text{day}} = \text{operating cost/year.}$$

A question was raised by one of the smelters as to this ground rule wherein input stream concentrations of 1.5% SO_2 or less was considered to be the maximum limitation before refrigeration equipment is required to maintain water balance in the acid plant. This number was somewhat arbitrarily chosen and depending upon the local conditions may be low. The curve in Figure 7 of this report illustrates the gas temperature or saturation temperature of the gas required to maintain a water balance for the production of either 93% or 98% acid versus SO_2 in the gas stream. This curve when extrapolated to the altitude of the Arizona smelters indicates that at 1.5% SO_2 a gas temperature in the vicinity of 60° is required for 93% acid. The cost for operation and capital for the refrigeration system assumed in this report was based on a system capable of reducing gas temperature to 40°F. Thus, it would seem that the requirement for maintaining water balance under Arizona conditions is achievable within the cost and schedule shown with the gas stream at 1.5% SO_2 and 60°F.

The SO_2 concentration range between 1.5 and 4% will require a gas temperature range from 60° to 85°F. Under some circumstances it may be necessary to have some additional refrigeration cooling within this range to maintain 93% acid concentration. If no refrigeration is used, a reduction in output acid concentration can occur. Humidity conditions, wherein evaporative cooling capability is not sufficient to maintain 93% acid product, occurs only occasionally. Without refrigeration during these periods the problem is to find a use for the more dilute material produced. Leaching, fertilizer production and agricultural land conditioning

can all use dilute acid (less than 93%). It is expected that this condition will occur only a small percentage of the time and will not have an effect on sulfur capture in the acid plant.

11. Acid plant capital cost (including installation) is based on scale factor of 0.6. See Figure 15.

12. If an acid plant is subject to above normal gas flow rates (see Figure 16) an increase in the capital cost for additional fan and duct work is included. It was assumed that 1/2 of the normal capital cost for a smelter acid plant goes to construction of the gas conditioning system of the plant.

$$\left(\frac{\text{SCFM}}{\text{Normal SCFM}}\right)^{.6} \times (1/2 \text{ of capital cost}) + (1/2 \text{ of capital cost}) = \text{total cost of upgraded plant}$$

13. If the acid plant input stream average exceeds 8.0% SO_2 a double contact acid plant will be installed.

14. Offgases from concentrator units are 100% SO_2.

15. For costing purposes, the oxygen injection equipment for oxygen enrichment is $250,000 to purchase and install and will not materially change within the capacity range required for the Arizona smelters. This equipment includes only that required to transfer the oxygen (by pipeline) from the source at the smelter property boundary to the point of use at the reverberatory furnaces (1000 ft.)

16. SO_2 concentrations used are averages. It is expected that variations will occur in reverberatory furnace and converter offgases. If concentration drops below the 3.5% to 4.0% level, operation of the preheater may be required. If low concentration occurs for 15 minutes or less, the thermal lag in the catalyst bed will compensate and the preheater will probably not be required. Therefore, no allowance for preheater operation under these conditions was made.

C. INDIVIDUAL SMELTERS

1. Review of Possible Control Approaches for Phelps Dodge/Morenci

The existing 600 TPD acid plant handling the roaster gases could be refurbished to minimize faulty equipment and maximize availability time.

The new single contact 2000 TPD acid plant has not completed the startup phase but is designed so that conversion to a double contact plant is possible. If any new control plans are instituted that allow relatively high SO_2 stream concentration (5% - 6% minimum) then this plant should be

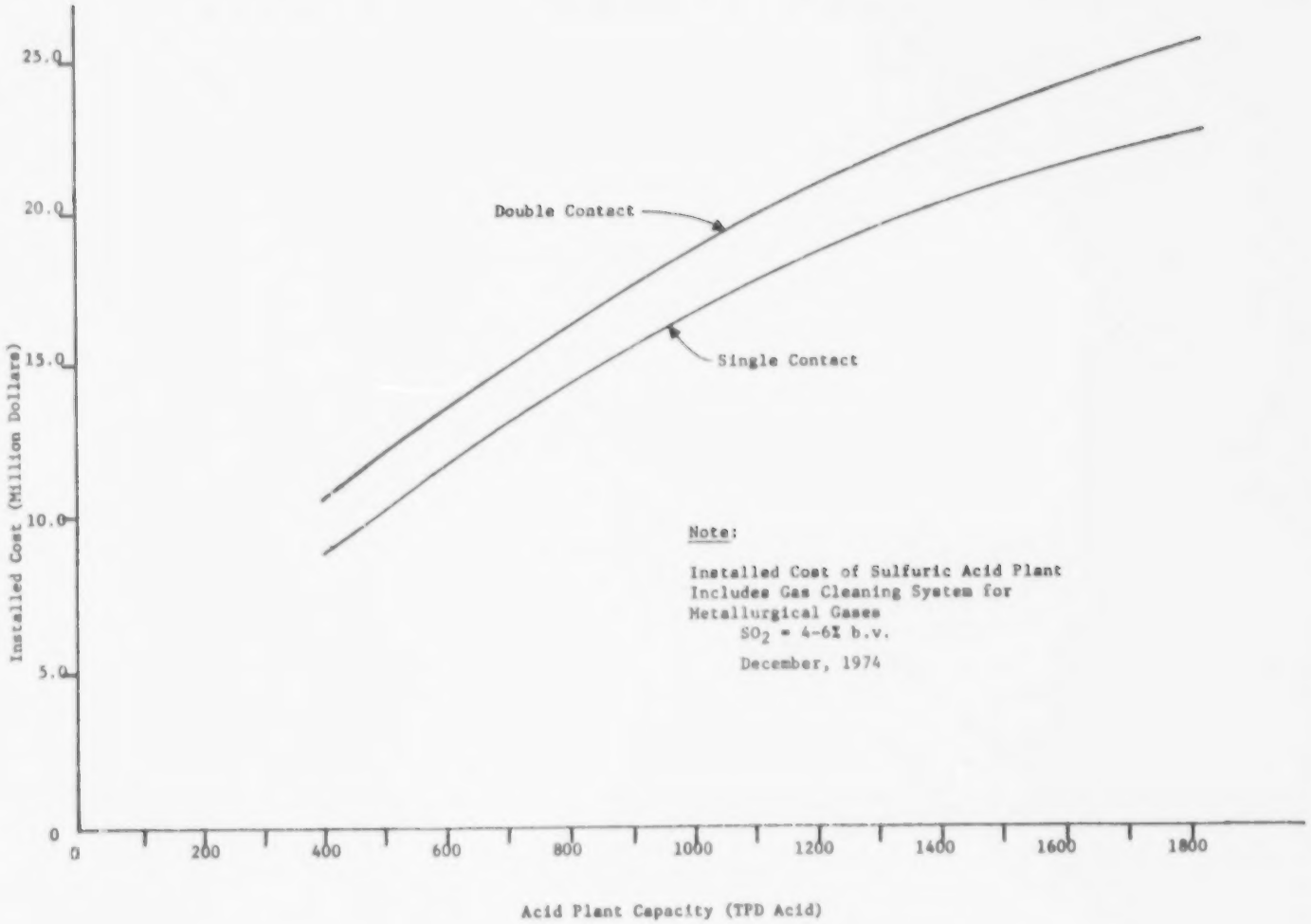


Figure 15. COST OF SULFURIC ACID PLANTS

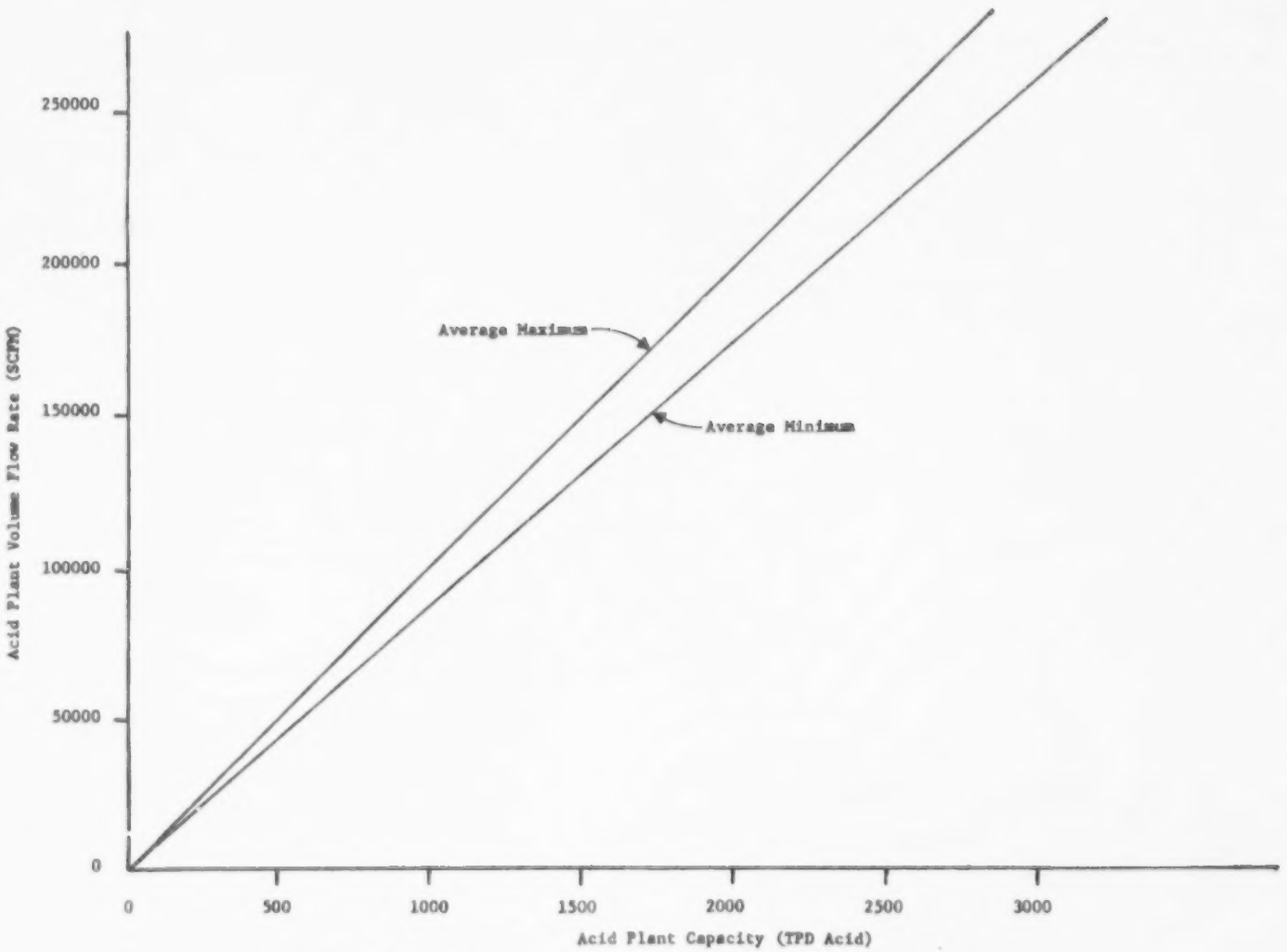


Figure 16. ACID PLANT VOLUME FLOW RATE VS. ACID CAPACITY

converted to double contact.

The new No. 5 reverberatory furnace is presently in the startup phase and once it is fully operating should be considered along with the other furnaces for some form of permanent control as noted in the following sections. There are no plans at the present for permanent control for the reverberatory furnaces.

With the installation of the new No. 5 furnace this smelter is committed, for at least the near future, to the use of this type of smelting device. As long as reverberatory furnaces are being used the addition of oxygen enrichment or concentration systems should be seriously considered as noted in the following section.

The major uncontrolled source of emissions at this smelter are the reverberatory furnaces. The major improvement in uncontrolled emissions can be obtained by controlling these devices. With both the roasters and converters emissions controlled by acid plants, total sulfur captured (once the new acid plant is in satisfactory operation) is a maximum of 62%. Approximately 28% of the sulfur is released and emitted from the reverberatory furnaces.

Alternative control plans are discussed below and are summarized in Table 2.

Alternative 1: Combining converter gases with No. 5 reverb

Combining the gases from the converters and the new No. 5 reverberatory furnace will result in a 2.95% SO_2 stream concentration at 357,200 SCFM. Additional acid plant capacity of 567 TPD will be required. The low SO_2 stream concentration will also require a preheater. A maximum of 87% sulfur capture can be accomplished by this approach.

It is estimated that a cost of slightly over $17,000,000 will be required for the additional acid plant capacity and the preheater. Operating cost of approximately $1,000,000 per year will be encountered due to preheater fuel requirements.

Alternative 2: Concentrating all reverberatory furnace gases and adding to converter gases

Concentrating all of the reverberatory furnace gases with a concentration system mixing this rich stream with the converter gases

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentration req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
1	Converter + #5 Reverb	567 (3167 Total)	357,200 SCFM @ 2.95% SO_2	Yes	No	851.4	88.1	$17,112,900 Operating Cost -- $1,092,000/ yr.	34 mo.
2	(All Reverb x Conc.) + Converter	836 (3436 Total)	Concentrator 282,000 SCFM @ 1.5% SO_2 / Acid Plant 121,500 SCFM @ 9.8% SO_2	No	Yes	939.5	0	$31,800,000 Convert to D.C., add capacity, concentrator	37 mo.
3	O_2 Enrichment for reverbs	836 (3436 Total)	<282,000 SCFM @ 4.0% SO_2	No	No	939.5	0	$15,250,000 Operating costs are subject to further development of this technique	36 mo
4	Roaster + # 5 Reverb + Converters	1101 (3101 Total)	381,200 SCFM @ 3.5% SO_2	Yes	No	851.4	88.1	$22,217,500 Operating cost -- $583,000/yr	37 mo.
5	Roaster + All Reverbs	1370 (3370 Total)	306,000 SCFM @ 2.3% SO_2	Yes	No	939.5	0	Not recommended	
6	Roaster + All reverbs + Converter	1370 (3370 Total)	423,000 SCFM @ 3.4% SO_2	Yes	No	939.5	0	Not recommended	

TABLE 2. ALTERNATIVE CONTROL PLANS
PHELPS DODGE/MORENCI

PACIFIC ENVIRONMENTAL SERVICES, INC.

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentration req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
7	(All Reverb) x concentrator + roaster + converter	1370 (3370 Total)	Concentrator 282,000 SCFM @ 1.5% SO_2 Acid Plant 145,500 SCFM @ 10.0% SO_2	No	Yes	939.5	0	$37,100,000 Convert to D.C. Add Capacity Concentrator	42 mo.
8	Converter only (S.C. to D.C. acid plant)	2000 (2600 Total)	117,200 SCFM @ 6.5% SO_2	No	No	666.4	273.1	$3,000,000 (Convert to D.C on new acid plant)	18 mo.
9	Roaster only (S.C. to D.C. acid plant)	600 (3100 Total)	42,000 SCFM @ 6.5% SO_2	No	No	666.4	273.1	$1,700,000 (Convert to D.C on old acid plant)	14 mo.
10	Reverb only	836 (3436 Total)	281,900 SCFM @ 1.5% SO_2	Yes	No	939.5	0	$27,975,000 Operating cost - $1,572,980/ yr.	37 mo.

TABLE 2. (Cont.) ALTERNATIVE CONTROL PLANS
PHELPS DODGE/MORENCI

will result in a 9.8% SO_2 stream concentration at a volume flow of 121,500 SCFM. Additional acid plant capacity of 836 TPD is required. The new acid plant plus the currently existing plant could be converted to a double contact for higher efficiency with the high SO_2 stream concentration. Maximum total sulfur capture can be obtained with this alternative. It is estimated that a capital cost of $31,800,000 will be required for the new acid plant capacity and the concentration system. A 37 month startup time is projected.

Alternative 3: Oxygen enrichment for the reverberatory furnaces

Using oxygen enrichment for the reverberatory furnaces will produce an SO_2 stream concentration of 4% or greater. This is sufficient to take the gases directly to a single contact acid plant. Additional acid plant capacity of 836 TPD will be required. Collecting the reverberatory gases will result in maximum total sulfur capture for this smelter. It is estimated that a capital cost of $15,250,000 will be required. Operating cost is subject to further development of this technique which will be required before it can be accepted for each smelter. A 36 month startup time is estimated.

Alternative 4: Combining the roaster, converters and the new No. 5 reverberatory gases

Combining the existing roaster and converter gases along with the new No. 5 reverberatory furnace gases will result in an SO_2 stream concentration of 3.5% at a total volume flow of 381,200 SCFM. An additional acid plant capacity of 1,101 TPD will be required. At this low average SO_2 stream concentration a preheater will also be required. Total sulfur capture in this technique will be a maximum of 87%. It is estimated that a capital cost of $21,000,000 will be required with an operating cost, primarily for the preheater of over $580,000 per year.

Alternative 5: Combining roaster gases with all reverberatory furnace gases

Combining the roaster gases with all the reverberatory furnace gases will result in an SO_2 stream concentration of 2.3% and a total gas volume of 306,000 SCFM. This will result in total maximum SO_2 capture, but the lower concentration will require a preheater. Because of the large volume flow and low concentration this plan is not recommended.

Alternative 6: Combining roaster, converter and all reverberatory furnaces

Combining the roaster, converters and all the reverberatory furnaces will result in a total gas volume flow of 423,000 SCFM and SO_2 concentration of 3.4%. This low stream concentration and high volume flow appears to be too costly to be economically feasible even though it would fix the maximum amount of sulfur.

Alternative 7: Concentrate the reverberatory gases and combine with the roaster and converter gases

Concentrating the reverberatory furnace gases and combining with the roaster and converter gases will result in a total volume flow of 145,000 SCFM at a 10.0% SO_2 stream concentration. This will allow the use of a double contact acid plant and will require an additional 1,307 TPD acid plant capacity. Maximum sulfur capture (up to 89%) will be accomplished using this alternative. It is estimated that approximately $37,000,000 capital cost will be required and will include conversion to double contact acid plants. This also includes all new acid plant capacity and the scrapping of the old acid plant. A 42 month time schedule to startup is expected.

Alternative 8: Convert the present 2,000 TPD new plant to a double contact

The present 2,000 TPD acid plant has the space and available foundations for converting to a double contact system. This will improve the sulfur capture by several percent but will still result in total sulfur capture of a maximum of 68%. It is expected that this will cost approximately $3,000,000 and take 18 months to completion.

Alternative 9: Converting existing acid plant to double contact will require an additional $1,700,000 and approximately 14 months for completion. Only several percent in sulfur capture will be gained.

Alternative 10: Collect reverberatory furnace offgases in present condition and pass directly to acid plant

Using the present offgases from the reverberatory furnaces at 1.5% SO_2 stream concentration and 281,900 SCFM supplied directly to a sulfuric acid plant can be accomplished and will require a preheater and refrigeration system. It is estimated that this will cost approximately $28,000,000 and result in an operating cost of nearly $1,500,000 per year. Startup time

is estimated to be 37 months. This will capture the maximum amount of sulfur.

2. Summary of Alternatives For Phelps Dodge/Morenci

With the use of reverberatory furnaces, oxygen enrichment is a potentially available technique that appears promising as an immediate and relatively rapid approach to collecting the reverberatory furnace offgases which are the major source of uncontrolled emissions.

The use of concentration systems should also be seriously considered as a potentially available technique for this smelter because of the obvious flexibility allowable with the high stream concentration.

The only difference between alternative 2 and alternative 7 is that the existing acid plant is scrapped in alternative 7 and replaced by the new plant capacity all double contact. Double contact acid plants, will improve conversion efficiency by approximately two percentage points.

3. Review of Possible Control Approaches for Phelps Dodge/Douglas

There are no existing or present plans for SO_2 permanent controls for the Douglas smelter. The smelter is presently working on tighter fitting hoods for the converters primarily for particulate control.

The largest amount of sulfur evolved is generated in the multiple hearth roasters. This is approximately 45% of the total sulfur entering the plant. The second largest source of sulfur is from the converter, approximately 32%. Present sulfur concentration in both the roaster and converter offgases is only 1.8% which is considerably lower than most smelters indicating large quantities of dilution air entering the system.

Repair and elimination of sufficient leakage in the roasters to upgrade the SO_2 gas does not appear feasible because of the condition of the roasters and associated duct work. Thus, it would seem that modification of the process either to go to "green" charge for the reverberatory or switch to fluid bed roasters would be very beneficial and practical for SO_2 permanent control.

The alternative approaches considered are shown in Table 3, will be discussed below.

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentrator req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
1	Converter only	753	87000 SCFM @ 4.4% SO_2	No	No	24	450.7	$14,750,000	36 months
2	Converter + 18 operating Roasters	1824	380,000 SCFM @ 2.5% SO_2	Yes	No	595.6	100.8	$32,737,500 Operating cost -- $1,540 000/yr	38 mo.
3	Roaster + Converter + 1 Reverb	1926.9	430,000 SCFM @ 2.3% SO_x	Yes	No	629.2	67.2	Not Recommended	
4	Roaster + Converter + 2 Reverb	2029.8	475,000 SCFM @ 2.2% SO_x	Yes	No	662.8	33.6	Not Recommended	
5	Roaster + Converter + 3 Reverb	2132.7	530,000 SCFM @ 2.1% SO_x	Yes	No	696.4	0	Not Recommended	
6	(Roaster + 3 Reverb) x Concentrator + converter	2133	Concentrator 440,500 SCFM @ 1.6% SO_2 / Acid plant 94,000 SCFM @ 11.5% SO_2	No	Yes	696.4	0	$39,000,000 D.C. acid plant concentrator	40 mo.
7	Converter + 1 Operating Roaster	812	103,000 SCFM @ 4.0% SO_2	No	No	265.1	431.3	$15,700,000	36 mo.

TABLE 3. ALTERNATIVE CONTROL PLANS
PHELPS DODGE/DOUGLAS

PACIFIC ENVIRONMENTAL SERVICES,

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentrator req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
8	Converter + 1 Reverb	855	140,000 SCFM @ 3.1% SO_2	Yes	No	279.3	417.1	$21,000,000 Operating Cost-- $419,000 /yr	36 mo.
9	Roaster x concentrator + 3 Reverb	1380	Concentrator 290,000 SCFM @ 1.7% SO_2 / Acid Plant 156,000 SCFM @ 4.5% SO_2	No	Yes	450.7	245.7	$32,000,000 S.C. Acid plant concentrator	38 mo.
10	Roaster x concentrator + 1 Reverb	1174	Concentrator 290,000 SCFM @ 1.7% SO_2 / Acid Plant 56,000 SCFM @ 12.6% SO_2	No	Yes	383.5	312.9	$32,200,000 D.C. Acid plant concentrator	38 mo
11	(O_2 enrichment x 3 Reverb) + converter	1061	4.1-4.3% SO_2 <243,000 SCFM	No	No	346.5	349.9	$17,450,000 Operating costs are subject to further development of this equipment	38 mo.

Table 3. (Continued) ALTERNATIVE CONTROL PLANS
PHELPS DODGE/DOUGLAS

Alternative 1: Converter Gases Only

A 753 TPD acid plant is required to handle gases generated from the converters only, assuming that the converter hoods have been installed to collect the normal amount of gas. It is expected that a gas stream concentration of 4.4% can be obtained. Total sulfur capture will be 32%.

Estimated cost for the 753 TPD acid plant is approximately $14,000,000 with a 36 month startup time from placing of the order.

Alternative 2: Combining Gases From Converters and Roasters

Combining the gases from the converters and the operating roasters (generally 18) will produce a total gas volume of 380,000 SCFM at 2.5% SO_2 concentration. This would require an acid plant of 1824 TPD capacity. With the low SO_2 concentration a continuously operating preheater would be required. Approximately 77% of the input sulfur would be captured using this approach.

Estimated cost for the 1824 TPD acid plant plus continuously operating preheater is approximately $25,000,000 with an operating cost of $1,549,000 per year consisting primarily of the fuel for the preheater. Installation time of 38 months is estimated.

With the low SO_2 stream concentration of 2.5% this approach becomes somewhat marginal particularly in view of the additional fuel cost required.

Alternative 3, 4 and 5: Combining Gases From Roasters Converters and Reverb.

These alternatives include combining the roaster, converter and reverberatory furnace gases either with 1,2 or 3 furnaces. The SO_2 concentration range varies from 2.1% to 2.3% and is considered too low to be practical particularly with the higher fuel requirements.

Alternative 6: Combining Roaster and Reverb Gases, Concentrating and Then Combining With Converter Gases

Combining the total roaster and reverberatory furnace gases and then passing these, at 440,500 SCFM and 1.6% SO_2 concentration to a concentration system. After concentration, then combining the essentially 100% SO_2 with the converter gas streams will result in a 11.5% SO_2 stream at 94,000 SCFM. This will lend itself to operation with a double contact sulfuric acid plant and will control 100% of the input sulfur except for fugitive

and other losses.

The 11.5% SO_2 stream will also allow the efficient use of the double contact sulfuric acid plant. The reduced volume flow of 94,000 SCFM will reduce the cost of this plant. It is estimated that a total cost for the concentration system and the 2133 TPD double contact acid plant will be approximately $31,000,000 and take 40 months to startup.

Alternative 7: Combining Converter Gases with One Roaster

Combining the converter gases with one operating roaster will provide a 4% SO_2 stream at 103,000 SCFM volume flow and allow operation with a single contact 812 TPD acid plant. Cost is estimated at $14,500,000 with a 36 month schedule. Maximum sulfur capture with this approach is 34% and does not appear to be worth doing compared to alternative number 1 with just converter gas capture.

Alternative 8: Combining Converter Gases with One Reverb

Combining the converter gases with one reverberatory furnace gas would result in a 3.1% SO_2 stream at 140,000 SCFM. This will provide 36% sulfur capture and cost approximately $16,000,000 if the gases are passed to an 855 TPD acid plant. 36 months is estimated as the startup time.

The problem here again is the use of additional fuel at a cost of $128,000 per year with continuous operation of a preheater in the acid plant. Fuel requirements may eliminate this approach.

Alternative 9: Concentration of Roaster Gases and Final Combination with All Reverb Gases

Combining the three reverberatory gases with roaster gases that have been passed through a concentrator will result in a 4.5% SO_2 stream at 156,000 SCFM. A 1,380 TPD acid plant is required. Concentration of the roaster gases will require a concentration system and a single contact acid plant of 1,380 TPD. Total sulfur capture will be approximately 58% with a 38 month schedule.

Alternative 10: Concentrated Roaster Gases Combined with One Reverb Gases

Combining one reverberatory furnace offgas stream with concentrated roaster gases will produce a 12.6% SO_2 stream at 56,000 SCFM. A

1174 TPD double contact plant will be required with a concentration system at a capital cost of $32,000,000. This approach will result in 50% sulfur capture with a 38 months schedule.

Alternative 11: Oxygen Enrichment of Reverb Combined With Converter Gases

Combining the oxygen enriched gases from the reverberatory furnace and the converter gases will result in a total volume flow less than 243,000 SCFM and a gas stream concentration of 4.1% to 4.3% SO_2. This will allow operation with a 1,062 TPD single contact acid plant and 45% sulfur capture. Costs are estimated to be $17,450,000 with 36 months to start up. Operating cost estimates are subject to further development of this technique.

4. Summary of Alternatives For Phelps Dodge/Douglas

The Phelps Dodge/Douglas smelter has no permanent SO_2 control and therefore, any efforts in this direction will result in an increase in sulfur capture.

The most obvious first area of control is the converters, since all copper smelters in Arizona except this one are currently controlling these emissions during blowing operations. Converter emission control alone will allow a maximum of 32% sulfur capture.

Control of SO_2 from the roasters, while requiring some development, will result in the greatest increase or a maximum of 45% sulfur capture. Roaster system repair or replacement or the installation of a concentration system is required.

Oxygen enrichment for the reverberatory furnaces, also requiring some development, is a possible approach for this smelter and could gain a maximum of 13% sulfur capture. This lower gain (because of low sulfur removal in the furnaces) would place this alternative on a lower priority than the above two.

5. Review of Possible Control Approaches For American Smelting And Refining Corporation (ASARCO/HAYDEN)

The amount of sulfur leaving the roasters, reverberatory furnaces and converters is shown in Table 1 indicating that the greatest percentage of sulfur is emitted from the converters with the multiple hearth roasters and reverberatory furnaces following in that order. Present SO_2 control is

only partially accomplished on the gases leaving the converters.

The present acid plant receiving converter gases has been almost a continuous problem since its startup in November 1971. For example, the acid plant was down the entire month of October and two weeks in November 1974 for repair. Furthermore, based upon the material balance it appears that the present acid plant of 750 TPD capacity is not sufficient to control the total amount of sulfur (296 TPD) being emitted from the converters. Additional acid plant capacity of 157 TPD is required to capture the total amount of sulfur being emitted from the converters. This is shown in Table 4 as alternative No. 1.

Increasing the capacity of the present acid plant should be possible and is shown as requiring a cost of approximately $6,000,000 and would require approximately 24 months time to accomplish. ASARCO is currently attempting to increase the capture capability of the existing acid plant by rework rather than adding equipment to increase capacity. (See discussion under Alternate 1).

There are presently no planned additional permanent control systems.

All except one of the present 12 multiple hearth roasters are in very poor condition and have large leakage sources. The company does not feel that the leaking roasters are repairable. Thus, because of the dilution air leakage, the output gases are only 2.5% SO_2 concentration and are not suitable to go directly to a conventional acid plant. Elimination of the roasters or replacement with fluid bed roasters would improve the offgas stream concentration and allow direct processing in an acid plant.

The ASARCO/Hayden smelter uses multiple hearth roasters to remove 25% of the sulfur from the input material, reverberatory furnace smelting to remove 18.5% of the sulfur and final converting to remove the remaining 55%. Table 4 summarizes alternative control plans.

ASARCO has commented on the values used to estimate gas volumes from the converters for evaluating various control alternatives. The average volume flow used of 100,000 SCFM is, of course, dependent upon how many converters are blowing. Since ASARCO has indicated that the acid plant is capable of handling the total converter flow and also that it is designed for 98,000 SCFM the value of 100,000 SCFM was considered representative. Also using the converter sulfur output of 315 TPD and 100,000 SCFM the SO_2 concentration calculates to be 4.6% which is a typical value that could be expected based

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentration req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
1	Converter only	157 (907 Total)	100,000 SCFM (Total) @ 4.6% SO_2	No	No	296	235	$5,200,000	24 mo.
2	Converter + All operating Roasters (8)	570 (1320 Total)	200,000 SCFM (Total) @ 3.35% SO_2	Yes	No	431	100	$14,656,100 (Operating cost $408,000/ Year)	36 mo.
3	Converters + 3 Roasters (Operating)	311 (1061 Total)	137,500 SCFM @ 4.0% SO_2	No	No	347	184	$8,500,000	32 mo.
4	Converters + 1 Reverb	310 (1060 Total)	210,000 SCFM @ 2.6% SO_2	Yes	No	346	185	$10,872,000 (Operating cost $856,000) /yr.	32 mo.
5	Converters + 2 Reverbs	463 (1213 Total)	320,000 SCFM @ 1.9% SO_2	Yes	No	396	135	$17,400,000 (Operating cost $1,630,000) /yr.	36 mo.
6	Converters + (Roasters + Reverbs) x concentrator	876	Concentrator 320,000 SCFM @ 1.14% SO_2 ---------- Acid Plant 103,700 SCFM @ 8.0% SO_2	No	Yes	531	0	$31,300,000 D.C. Acid Plant (new), convert old plant to D.C. Concentrator	40 mo.

TABLE 4. ALTERNATIVE CONTROL PLANS
ASARCO/HAYDEN

PACIFIC ENVIRONMENTAL SERVICES, INC.

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentration req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
7	(Roaster x Conc.) + 2 Reverb.	720 (1470 Total)	Concentrator 100,000 SCFM @ 2.5% SO_2 / Acid Plant 222,100 SCFM @ 1.6% SO_2	Yes	Yes	349	182	Not recommended	
8	(Roaster x Conc.) + 1 Reverb	720 (1470 Total)	Concentrator 100,000 SCFM @ 2.5% SO_2 / Acid Plant 112,000 SCFM @ 2.6% SO_2	Yes	Yes	299	182	Not recommended	
9	(Reverb x Conc.) + Roasters	720 (1470 Total)	Concentrator 220,000 SCFM @ 0.7% SO_2 / Acid Plant 101,600 SCFM @ 3.6% SO_2	Yes	Yes	349	182	Not recommended	
10	O_2 Enrichment of Reverb	306 (1056 Total)	4.0% SO_2 220,000 SCFM	No	No	214	317	$7,750,000 Operating costs are subject to further development of this technique	34 mo.

TABLE 4 (Cont) ALTERNATIVE CONTROL PLANS
ASARCO/HAYDEN

PACIFIC ENVIRONMENTAL SERVICES, INC.

on the industry experience and desirable acid plant input. Furthermore data sent to Carl Billings in letter from ASARCO (J.J. Winkel) dated December 8, 1970 states " ...three units (converters) should be blowing most of the time. Assuming an average tuyere air flow of 20,000 SCFM plus 50% inspirated ambient air at the hood the...total volume to the flue system is 30,000 SCFM per operating converter" (or 90,000 SCFM total). The same letter also indicated the acid plant was designed for 98,000 SCFM and is capable of accepting all of the converter gas.

Variation of SO_2 concentration is recognized as a potential problem and must be considered in sizing equipment. Tightening up the gas collection system with hood improvement and leak elimination along with providing additional SO_2 for injection to upgrade low concentration conditions will minimize this effect. Concentration systems or sulfur burners are sources of readily available SO_2.

Alternative 1: Increase Acid Plant Capacity to Handle Total Converter Gas Flow

As discussed above, the present existing acid plant would need to be increased in capacity to handle the total amount of sulfur being emitted from the present converter systems. It is expected that this would capture an additional 51 TPD of sulfur.

It should be noted here that there is usually additional capacity built into an existing acid plant and, if the unit is in good condition, additional capacity can be generated. This coupled with the flow variation from the converter line indicates the possibility that the existing acid plant might under most conditions, be capable of handling the maximum flow from the converter depending upon how the converter blowing times are scheduled. Therefore, the additional plant capacity and cost estimate would represent an upper limit to the smelter to accomplish complete converter offgas control. (ASARCO stated at a meeting on March 10, 1975 at EPA offices in San Francisco that modifications to the plant are currently under way and that they expect it to be capable of handling all of the converter gases by the end of 1975).

Alternative 2: Combine Converter and Roaster Gases

This alternative consists of combining the converter gases with the eight operating roaster gases. This results in essentially doubling the

gas flow rate to 200,000 SCFM and reduces the average SO_2 stream concentration to 3.35%. At this low average stream concentration, it will probably be necessary to operate the preheater more continuously for acid plant operation. The percentage SO_2 stream fluctuation will vary primarily depending upon the converter blowing time and scheduling. Additional acid plant capacity of 570 TPD will be required to handle the total amount of sulfur. This approach will increase the sulfur capture and result in escape of only that generated in the reverberatory furnace. A cost of $13,000,000 is estimated to include the additional acid plant capacity and preheater. Operating cost of $408,000 per year is estimated to be the cost of fuel for the preheater and does represent an increase in energy requirement. Roaster gas may also cause dark acid to be produced because of the flotation reagent present in the feed material. Dark acid has a more limited market but still can be used in many applications such as ore leaching or fertilizer production.

Alternative 3: Combining Gases from the Converters and Three Roasters

Combining the converters with sufficient number of roasters to produce an SO_2 stream concentration of 4.0% considered to be the minimum for single contact autogenous operation will result in combining three operating roasters. This approach will eliminate or minimize the requirement for the preheater and still improve the sulfur capture to a maximum of 65%. An increase in acid plant capacity of 311 TPD is required to handle a total gas stream of 137,000 SCFM at 4.0% SO_2. An estimated capital expenditure of $8,000,000 to cover the additional acid plant capacity could be installed in approximately 32 months.

Alternative 4: Combining Gases From the Converter With One Reverb.

Combining the converter offgas with the offgas from one reverberatory furnace will result in an SO_2 stream concentration of 2.6% and a volume flow of 210,000 SCFM. This will improve the sulfur capture to about the same point as alternative number 3 and will result in the requirement for continuous operation of the preheater in the acid plant. A $9,500,000 initial cost and an operating cost of $856,000 per year with increase in the energy requirement is estimated. A 32 month installation and startup schedule is estimated.

Alternative 5: Combine Gases from the Converter and Two Reverbs.

Combining gases from the converters and the two reverberatory furnaces results in an increase of sulfur capture to a maximum of 73% of the input sulfur. However, the gas stream concentration drops to 1.9% SO_2 which requires an increase in the preheater capacity and operating cost. A $11,500,000 initial cost with operating cost of $1,630,000 per year and a 36 month installation schedule is estimated.

Alternative 6: Concentrate Reverb and Roaster Gases and Combine with Converter Gases

This alternative consists of combining the gases from the reverberatory furnaces and roasters and passing them through a concentration system to upgrade for mixing with the converter gases to apply directly to an acid plant. The concentrator will generate essentially a pure SO_2 stream. This results in an 8.0% SO_2 stream concentration and is directly applicable to a double contact sulfuric acid plant. Maximum sulfur capture can be accomplished with this technique. Initial capital cost is estimated to be $31,300,000 assuming a new double contact acid plant, converting the existing acid plant to double contact and the concentration system. 40 months to startup is estimated, however, with proper planning some of these systems can be placed in operation before the total complex is available.

Alternative 7: Concentrate Gases from the Roasters and Combine with Two Reverbs

Combining the gases from two reverberatory furnaces with concentrated roaster gases will result in an SO_2 concentration of 1.6% which is not high enough to justify this approach in view of the other alternatives. Alternatives 7 through 10 include handling the converter gases through the presently existing acid plant.

Alternative 8: Concentrate Roaster Gases and Add to One Reverb.

Passing the roaster gases through a concentration system and adding the gases from one of the reverberatory furnaces results in an SO_2 stream concentration of 2.6% which is not sufficiently attractive to pursue.

Alternative 9: Concentrate Reverb Gases and Mix with Roaster Gases

Taking the gases from the reverberatory furnace and passing them through a concentration system and then adding this to the roaster gases will result in a 3.6% SO_2 stream concentration. Again this does not appear to be an effective method of control in view of the alternatives.

Alternative 10: Oxygen Enrichment for Reverbs

Using oxygen enrichment for the reverberatory furnace will increase the SO_2 stream concentration to a minimum of 4.0%. This will allow passing of the gases from the reverberatory furnace to a single contact acid plant. It is expected that an additional $8.250,000 will be required to include the oxygen enrichment system and the additional 306 PTD acid plant capacity required.

6. Summary of Alternatives For American Smelting And Refining Corporation (ASARCO/HAYDEN)

Upgrading of the present acid plant to allow complete collection of SO_2 from the converters appears possible and is presently being attempted by ASARCO.

The major problem with the ASARCO/Hayden smelter is that the multiple hearth roasters produce a very low stream concentration of SO_2 primarily because of their mechanical condition and the considerable dilution air entering the system at this point. While the reverberatory furnace problem is the same at this smelter as with the others the roasters also represent a similar SO_2 control problem.

Thus, it appears that either replacement or elimination of the present roasters or passing the roaster and reverberatory furnace offgases to a concentration system is the most logical approach for this smelter.

Oxygen enrichment of the reverberatory furnace and perhaps even the multiple hearth roasters is a possibility but is not as promising a technique for this particularly smelter as is the concentration or equipment modification route because of the dual problem. Little experience is available on roaster oxygen enrichment.

7. Review of Possible Control Approach For Magma Copper Company/ San Manuel

Magma/San Manuel has three reverberatory furnaces and six converters. Present and planned SO_2 control capability includes control of all of the gases from the converters by an acid plant.

There are no present plans for controlling the reverberatory furnace gases. Any additional significant increase in SO_2 control must be focused upon the gases coming from the reverberatory furnaces. The following sections consider this basic approach with alternatives.

If energy supplies become more critical in the future, the smelter may be forced to use alternate fuels such as heavy oil (Bunker C) and coal, in their reverberatory furnaces or use oxygen enrichment techniques.

The current smelting process takes green charge directly to the reverberatory furnaces and then processes the matte in the converters to obtain blister copper. A summary of the control plans considered is shown in Table 5 and are discussed by alternatives in the following:

Alternative 1: Combine Converter and Reverb Gases

Combining the converter gases with the gases from the three reverberatory furnaces will result in an average SO_2 stream concentration of 3.1% with 471,000 SCFM of gas. This stream concentration is not sufficient to operate even a single contract acid plant autogenously and will therefore, require a preheater. The preheater must operate at those times when the SO_2 concentration is below 3.5%. Also, the large gas volume flow rate will require a more costly gas handling system.

Controlling the gases from the converter and all of the reverberatory furnaces will essentially control all of the sulfur input except for fugitive emissions as compared to a maximum of 69% sulfur capture if converter gases only are controlled as presently planned.

It is estimated that a capital cost of $20,870,000 is required to provide the additional acid plant capacity and preheater capability. Yearly operating cost is estimated to be $1,440,000 which represents the fuel cost for the preheater. The time from order placement to start-up is estimated to be 36 months.

Alternative	Gas Streams combined	Acid Plant Cap. needed (TPD)	Stream Characteristics	Preheater req'd	Concentration req'd	Total Sulfur Captured (TPD)	Sulfur (TPD) Escaping (Roaster, Reverb, Converter)	Cost	Time Schedule
1	Converter + 3 Reverbs	793 (2817 Total)	471,000 SCFM @ 3.1% SO_2	Yes	No	920	0	$20,870,000 Operating Cost $1,440,000/yr	36 mo.
2	(3 Reverb) x Conc. + Converter	793 (2817 Total)	Concentrator 284,000 SCFM @ 1.5% SO_2 Acid Plant 191,000 SCFM @ 7.5% SO_2	No	Yes	920	0	$30,500,000	36 mo.
3	O_2 Enrichment for 3 Reverb	793 (2858 Total)	< 284,000 SCFM 4.0% SO_2	No	No	920	0	$14,550,000 Operating costs are subject to further development of this technique	38 mo.
4	Converter + 1 Reverb	264 (2290 Total)	282,000 SCFM @ 4.1% SO_2	No	No	747	173	$7,000,000	32 mo.
5	Converter + 2 Reverb	529 (2554 Total)	377,000 SCFM @ 3.4% SO_2	Yes	No	834	86	$15,322,500 Operating cost --$768,000/yr	34 mo.
6	3 Reverbs	793 (2858 Total)	284,000 SCFM @ 1.5% SO_2	Yes	No	920	0	$28,152,000 Operating Cost -- $1,577,500/yr.	38 mo.

TABLE 5. ALTERNATIVE CONTROL PLANS
MAGMA/SAN MANUEL

PACIFIC ENVIRONMENTAL SERVICES, INC.

Alternative 2: Concentration of Reverb Gases and then Combining with Converter Gases

Combining the converter gases with gases from the three reverberatory furnaces that have been passed into a concentration system will result in a 7.5% SO_2 stream at 191,000 SCFM. This double contact acid capacity must be included along with conversion of present plant to double contact.

It is estimated that a capital cost of $30,500,000 will be required which includes the additional acid plant capacity and the concentration system. Installation time of 36 months assumes that the acid plant and concentration systems will be installed simultaneously.

Alternative 3: Oxygen Enriched Reverb Gases to an Acid Plant

Using oxygen enrichment for the three reverberatory furnaces will produce a furnace offgas of at least 4.0% of SO_2 concentration which will allow processing of these gases directly in a single contact acid plant. A reduction in the gas volume flow will also result and provide a somewhat smaller or lower cost acid plant.

The acid plant and oxygen enrichment system costs are estimated to be $14,550,000 with operating costs subject to further development of this technique.

Alternative 4: Combining Converter Gases with One Reverb Gas

Combining the converter gases with one reverberatory furnace will result in a maximum of 81% sulfur capture. A 4.1% SO_2 stream concentration at 282,000 SCFM will result with this gas combination. This concentration is sufficient to pass the gases directly to a single contact acid plant.

It is estimated that the additional 264 TPD acid plant capacity will cost $7,000,000 and take 32 months for installation.

Alternative 5: Combining Converter Gases with Two Reverb Gases

Combining the converter gases with gases from two of the reverberatory furnaces will result in a stream concentration of 3.4% at 377,000 SCFM. This concentration will require the use of a preheater and an added 529 TPD acid capacity. Sulfur capture will be a maximum of 90.6%.

Estimated capital cost of $15,320,000 and an operating cost of $768,000

per year representing fuel cost for the preheater. A 34 month installation time is estimated.

Alternative 6: Present Reverb Gas Stream Processing with an Acid Plant

Combining the reverberatory gases at their present 1.5% SO_2 stream concentration and 284,000 SCFM and passing them to a sulfuric acid plant will require a continuous preheater and probably a refrigeration system. (See Section IV).

Capital cost for installation of this equipment including a preheater, a refrigeration system and a single contact 793 TPD acid plant is estimated to be $28,152,000 with an operating cost of $1,454,250 per year and an installation time of 37 months.

This will result in a maximum total input sulfur capture except for fugitives.

8. Summary of Alternatives For Magma Copper Company/San Manuel

The capture of sulfur from the gases of the three reverberatory furnaces are the remaining uncontrolled problem for this smelter. Oxygen enrichment plus additional acid plant capacity appears to be an attractive approach. This would require a relatively low capital expenditure and provide nearly 100% sulfur capture.

The second alternative that appears promising is to concentrate the reverberatory gases in a concentration system to also obtain essentially 100% sulfur input capture. The two approaches of the concentration system and the oxygen enrichment are considered potentially available technology. See Section IV.

The third approach will simply combine all of the gases which will result in a 3.1% SO_2 stream. This stream concentration is marginal in terms of autothermal operation and will require a preheater probably operating continuously. Total gas flow rate is very high which requires high capacity systems.

LIST OF REFERENCES

1. "Facing tne Change in Copper Technology" Engineering & Mining Jrnl, April 16, 1973

2. "Background Information - Proposed New Source Performance Standards For Primary Copper, Zinc, and Lead Smelters" EPA Document, Office of Air and Water Programs, Research Triangle Park, North Carolina

3. "Reverberatory Matte - Smelting Process" U.S. Patent 3,222,162 G.C. Beals, J. Kocherhans, and K.M. Ogilvie assigned to Kennecott Copper Corp; New York, N.Y. December 7, 1965

4. "Operation of Reverberatory Furnaces on Air-Oxygen Blasts" Y.P. Kupryakov, The Soviet Jrnl. of Non-Ferrous Metals

5. "Tonnage Oxygen For Nickel And Copper At Copper Cliff" R. Saddington, W. Curlook, P. Queneau, Jrnl. of Metals, Vol. 18 April 1966, Pg. 440-452

6. "Oxygen Utilization In The Copper Reverberatory Furance: Theory And Practice" P. Wrampe, E.C. Nollmann, Union Carbide Corp., Linde Division, Los Angeles, California

7. "Possibilities For Technical Progress In Reverberatory Smelting Of Copper Concentrates" V.I. Smirnov, The Soviet Jrnl. of Non-Ferrous Metals

8. "Present State Of The Problem Of The Use Of Oxygen-Enriched Air In Non Ferrous Metallurgy" D.D. Chizhikov, A.A. Bsikov Metallurgical Institute, Academy Of Sciences Of The USSR. (Source unknown)

9. "An Evaluation Of Tonnage Oxygen Plants" S. Katell, P. Wellman, Bureau of Mines, U.S. Dept. of Interior, Morgantown, West Virginia

10. "Sulfuric Acid Plants For Copper Converter Gas" J.B. Rinckhoff ACS Paper, April 4, 1974

11. "The Manufacture Of Sulfuric Acid" W.W. Duecker, J.R. West, ACS Monograph No. 144, Reinhold Publishing Corp., 1959.

APPENDIX A

Copper Smelting Process

The basic copper smelting process starts with concentrated raw material which is usually chalcopyrite, $CuFeS_2$, a copper iron sulfide. This material is mixed with fluxes and recycled material and processed to reduce the iron to iron sulfide and the copper to copper sulfide. This can be done in two stages or one stage by using a roaster and reverberatory furnace or just a reverberatory furnace. Roasting drives off a portion of the sulfur from the concentrate which is then fed as calcines to the reverberatory furnace.

Smelting of calcines from the roasters in oil or natural gas fired reverberatory furnaces produces a lighter liquid slag composed of mainly iron, calcium and aluminium oxide silicates with a copper content ranging between 0.4 and 1.0% copper and a heavier layer of matte typically composed of 30% copper, 39% iron and 26% sulfur. A copper content of about 30% in the matte is desirable because a higher percentage results in a higher percentage of copper retained in the furnace slag, while a lower percentage requires more oxidation of the iron and sulfur in the matte during the subsequent and more expensive converting stage. Sulfur elimination in the roaster and reverberatory furnace is balanced to obtain the most economic matte grade.

Molten matte is poured into two or more Peirce-Smith converters - horizontal, cylindrical basic-lined vessels, typically 13 feet in diameter and 30 to 32 feet long. Flux containing preferably 70% to 80% silica is added and air is blown into the matte through submerged pipes called tuyeres to oxidize the iron and sulfur content of the matte. The iron oxide formed combines with the silica flux to produce an iron silica slag that is skimmed off. Molten temperatures of 2,100 to 2,200^{o}F the reaction of

oxygen with iron and sulfur is exothermic and regular additions of cold copper bearing materials are required to limit converting temperatures.

All but 1% or 2% of the iron and a considerable portion of the sulfur is oxidized prior to skimming off the iron silicate slag, leaving a "white metal", about 70% copper and 24% sulfur. Further blowing converts most of the remaining sulfur to SO_2 leaving a final blister copper usually containing about 98.5% to 99.3% copper, 0.3% sulfur, some dissolved oxygen, and other impurities. The 40-50 ton converter charge of blister may be further refined in a reducing atmosphere and either cast into cakes for shipment or into anodes for treatment and electrolytic refining. (Reference 1).

APPENDIX B

Visits to Arizona Copper Smelters and Arizona Department of Health

1. Visit to American Smelting and Refining Corporation at Hayden, Arizona

A visit was made to the American Smelting and Refining Corporation (ASARCO) smelter at Hayden, Arizona on August 16, 1974, to discuss SO_2 control and inspect the smelter.

Those present were:

Jack Winkel, Smelter Manager (Mr. Cahill now Manager)

Mel Sharpe, Smelter Superintendent

Charles Counts, Smoke and Fume Department, ASARCO Central Engineering, Salt Lake City

Red Guptill, Meteorologist

Visitors

Phillip Wondra, EPA Region IX

Mead Stirland, Arizona Board of Health

I.J. Weisenberg, PES

A second visit was made on October 22, 1974 to observe the smelter in operation since they were on strike during the first visit.

Visitors

Charlotte Hopper, EPA

Meade Stirland, State of Arizona

I.J. Weisenberg, PES

2. Visit to Magma Copper Company, San Manuel

A visit was made July 18, 1974 to the Magma Copper Company at San Manuel, Arizona to discuss SO_2 collection and review the smelter equipment.

Those present were:

Phillip Wondra, EPA Region IX, Contract Officer

Geoffrey Grubbs, EPA, DSSE (Enforcement) Washington D.C.

Mead Stirland, Engineering Services Section, Bureau of Air Pollution Control, State of Arizona

E.K. Staly, General Manager

John D. McIver, Manager of Smelting and Refining

Richard Sloan, Smelter and Acid Plant Superintendent

Stoker, Acid Plant Foreman

I.J. Weisenberg, PES

A second visit was made on October 22, 1974 to observe the smelter in operation since they were on strike during the first visit.

Visitors

Charlotte Hopper, EPA

Meade Stirland, State of Arizona

I.J. Weisenberg, PES

3. Visit to Phelps Dodge/Douglas

A visit was made to the Phelps Dodge/Douglas, Arizona Copper Smelter on August 8, 1974 to discuss operation of plant, SO_2 Control Procedures and to inspect the equipment. Those present were:

Don Carey, EPA Washington D.C.
Phillip Wondra, EPA Region IX, San Francisco
Fred Porter, EPA Durham, No. Carolina
Bill Polglase EPA Durham, No. Carolina
Meade Stirland, State of Arizona
I.J. Weisenberg, PES
Walter Gage Phelps Dodge Smelter Superintendent
Dick Ivanicky, Phelps Dodge Smelter General Foreman

The Phelps Dodge Western Engineering Group is located at Douglas. Jack Davis is Chief Engineer.

Fred Hoffman, Phelps Dodge Western Engineering was also questioned in the afternoon meeting.

4. Visit to Phelps Dodge/Morenci, Arizona Copper Smelter

A visit was made to the Phelps Dodge/Morenci, Arizona Copper smelter on August 6th and 7th 1974. Those present were as follows:

Phelps Dodge

John O'Neil Smelter Manager
John Bolles, Smelter General Superintendent
Stuart Towle, Smelter Superintendent
Bob Rose, Assistant Smelter Superintendent
Dr. Dick Mead, Metallurgist
Ron Riggs, Acid Plant Manager

Visitors

Jim Casey, EPA Washington D.C.
Don Carey, EPA Washington D.C.
Fred Porter, EPA Durham, No. Carolina
Bill Polglase EPA Durham, No. Carolina

Meade Stirland, State of Arizona

I.J. Weisenberg, PES

A second visit was made on October 23, 1974 to observe the smelter in operation since they were on strike during the first visit.

Visitors

Charlotte Hopper, EPA

Meade Stirland, State of Arizona

I.J. Weisenberg, PES

The following smelter visits were made to consider fugitive emissions only.

5. Visit to Phelps Dodge/Ajo

A visit was made to the Phelps Dodge/Ajo, Arizona smelter on July 25, 1974 to obtain equipment and operating data, to determine available emissions.

Those present were the following:

Phelps Dodge

R.H. Orr, Manager

F.R. Rickard, Smelter Superintendent

J.N. Sudler, Chief Engineer

G. Perry, Supervisor Smelter System

Visitors

M. Stirland, State of Arizona

P. Wondra, EPA

I. Weisenberg, PES

6. Visit to Kennecott Copper Smelter Hayden, Arizona

The Kennecott Copper Smelter at Hayden, Arizona was visited on 24 July 1974 to obtain plant design and operating information.

Those present were:

Kennecott Copper

Ivor [illegible]kering, General Manager

Tom Bethard, Smelter Metallurgist

Clint Fitch, Environmental Control

Stuart Nebeker, Reduction Plant Supervisor

Joe Mortimer, Safety & Environmental Control Manager (Not present)

Visitors

P. Wondra, EPA, Region IX, San Francisco

Meade Stirland, State of Arizona Health Department

I.J. Weisenberg, PES

7. Visit to Inspiration Copper Company, Miami, Arizona

The Inspiration Consolidated Copper Company Smelter at Miami, Arizona was visited on July 17, 1974.

Those present were:

P. Wondra, EPA Region IX, Contract Officer

Geoffrey Grubbs, EPA, DSSE (Enforcement) Washington D.C.

Meade Stirland, Engineering Services Section, Bureau of Air Pollution Control, State of Arizona

William (Bill) Pattulo, Director of Environmental Services, ICCC.

I.J. Weisenberg, PES

8. Visit to State of Arizona Department of Health to Obtain Copper Smelter Data

A visit was made on 7/10/74 and 7/11/74 to the Engineering Services Section, Bureau of Air Pollution Control, Environmental Health Services, Arizona Department of Health Services, 1740 West Adams Street, Phoenix, Arizona to obtain copper smelter data from their files. Most of the data were obtained from material submitted with individual smelter compliance plans and drawings.

Mr. Carl Billings, Manager directed the collection of data by I.J. Weisenberg, PES.

APPENDIX C

Alternative Control Plans, Operating Conditions and Cost Estimate Calculations

ALTERNATIVE CONTROL PLAN INFORMATION

PHELPS DODGE/MORENCI

1. Combine #5 reverb offgas with converter offgas in present 2000 TPD acid plant with added capacity #5-240,000 SCFM @ 12% SO_2

Total Sulfur input $492 + (240{,}000 \times .012) \times \frac{1440}{11.2 \times 2000} = 677.1$ TPD-S

Total flow rate = 357,200 SCFM

This implies 2.95% SO_2 concentration

This implies necessity of additional preheating cap.

Acid plant cap needed $= 185.1 \times \frac{98}{32} = 567$ TPD acid

Cost -- S.C. 567 TPD acid plant = $12,300,000

additional preheater cost = 1,845,000 (15%)

additional flow cap cost 2,867,900

$17,012,900 Total

Operating cost $= \frac{357.2}{85} \times 433 \times .60 =$ 1,092,000/yr (Preheater)

2. Route reverb offgas thru concentrator, combine with converter offgas, then route into present 2000 TPD acid plant with added capacity.

Total sulfur input = 273.1 + 492 = 765.1 TPD-S

Total flow rate $117{,}200 + \frac{273.1 \times 11.2 \times 2000}{1440} = 121{,}500$ SCFM

This implies 9.8% SO_2 concentration

This implies D.C. acid plant may be used

Acid plant cap. needed $= 273.1 \times \frac{98}{32} = 836$ TPD acid

Cost --

Convert 2000 TPD plant to D.C.	$3,000,000	
D.C. 850 TPD plant	16,800,000	
Concentrator	12,000,000	
	$31,800,000	Total

3. Use O_2 enrichment on reverb offgas, combine with converter gas, and route to 2000 TPD acid plant with added cap.

Total sulfur input = 765.1 TPD-S

Total flow rate = about 260,000 SCFM

This implies - 4.0% SO_2 conc.

Acid plant cap. needed = $273.1 \times \frac{98}{32}$ = 836 TPD acid

Cost --

S.C. 850 acid plant	$15,000,000	
O_2 injection equipment	250,000	
	$15,250,000	Total

Operating cost for O_2 and fuel may be determined by future development of this technique.

4. Combine Roaster with #5 reverb and converters and route into 2000 TPD acid plant with additional capacity.

Roaster offgas = 24000 SCFM @ 11.3% SO_2

#5 Reverb offgas = 240,000 SCFM @ 1.2% SO_2

Total Sulfur input = $492 + 185.1 + \frac{(24000 \times .113) \times 1440}{11.2 \times 2000}$

= 851.4 TPD

Total Flow = 117,200 + 240,000 + 24,000 = 381,200

This implies 3.5% SO_2

This implies necessity of additional preheater cap.

Acid plant cap. needed = $359.4 \times \frac{98}{32}$ = 1101 TPD acid

Cost --

S.C. 1100 TPD acid cost	=	$17,700,000	
Additional preheater cost	=	2,655,000	(15%)
Additional flow cap cost	=	1,862,500	
		$22,217,500	Total

Operating cost = $\frac{381.2}{85}$ x 433 x .30 = $583,000/yr (Preheater)

5. Combine roaster and all reverbs, route to new acid plant

   Total sulfur input to new plant = 174.4 + 273.1 = 447.5 TPD-S

   Flow = 24,000 + 282,000 = 306,000 SCFM

   This implies 2.3% SO_2 concentration

   This alternative is not recommended due to low % SO_2

6. Combine roaster, converter, and all reverb gases and route to new acid plant.

   Total sulfur input = 174.4 + 273.1 + 492 = 939.5 TPD-S

   Flow = 24,000 + 282,000 + 117,000 = 423,000 SCFM

   This implies 3.4% SO_2 concentration

   This alternative is not recommended due to low % SO_2

7. Concentrate reverb gas, combine concentrated stream with converter adn with roaster offgases offgases, route to 2000 TPD acid plant with added cap.

   Total sulfur input -- 939.5 TPD-S

   Total Flow = 117,200 + $\frac{273.1 \times 11.2 \times 2000}{1440}$ + 24,000 = 145,500

   This implies 10.0% SO_2 conc.

   This implies that D.C. acid plant can be used.

   Acid plant cap needed = 1370 TPD acid

   Cost --

Convert 2000 TPD to D.C.	=	$3,000,000

	B/fwd	3,000,000	
1370 TPD D.C. Acid Plant	=	$22,100,000	
Concentrator	=	12,000,000	
		$37,100,000	Total

8. Convert 2000 TPD acid plant from S.C. to D.C.
   D.C. acid plant conversion $ 3,000,000 Total

9. Convert 600 TPD acid plant from S.C. to D.C.
   D.C. acid plant conversion $1,7000,000 Total

10. Route reverb gases to a new acid plant with continuous preheating and refrigeration

    Sulfur input to plant - 273.1 TPD-S

    Flow into plant - 281,900 SCFM

    This implies need for continuous preheating and refrigeration

    Necessary acid plant capacity = $273.1 \times \frac{98}{32} = 836$

    Cost --

836 TPD S.C. acid plant	=	$15,000,000	
preheater/refrig cap	=	4,500,000	
additional flow cap	=	8,475,000	
		27,975,000	Total

Operating costs — $\frac{282}{85} \times 433{,}000 \times 1.0 = 1{,}436{,}540$ (PHTR)

$\frac{836}{900} \times 340 \times 24 \times 18 = 136{,}440$ (REFRIG)

$1,572,980/yr

ALTERNATIVE CONTROL PLAN INFORMATION

PHELPS DODGE/DOUGLAS

ASSUME: The converter offgas handling system can be sufficiently repaired to give a 4.4% SO_2 stream.

1. Route converter offgas to an acid plant

   Sulfur input = 245.7 TPD-S

   Flow = 87,000 SCFM

   This is what is necessary for a 4.4% SO_2 concentration

   Acid plant cap. needed = $245.7 \times \frac{98}{32}$ = 753 TPD acid

   Cost --

   750 TPD S.C. acid plant = $13,800,000

   $\left(\frac{87}{70}\right)^{.6} \times 6{,}900{,}000 - 6{,}900{,}000$ = flow cap. additional = 950,000

   14,750,000

2. Combine Roaster and converter offgases and route to acid plant

   Sulfur input = 245.7 + 349.9 = 595.6 TPD-S

   Flow = 87,000 + 290,000 = 377,000 SCFM

   This implies a 2.5% SO_2 conc.

   This implies that preheater capac. must be added

   Acid plant cap. needed = $595.6 \times \frac{98}{32}$ = 1824 TPD acid

   Cost --

   1825 TPD S.C. acid plant = $22,500,000

   Add'l preheater cap. = 3,375,000 (15%)

   $\left(\frac{377}{170}\right)^{.6} \times 11{,}250{,}000 - 11{,}250{,}000$ = flow cap 6,862,500

   32,737,500

   Operating cost = $\frac{377}{85} \times 433{,}000 \times .80$ = $1,540,000/yr (Preht.)

3. Roaster + Converter + 1 Reverb to acid plant

Sulfur input = $245.7 + 349.9 + \frac{100.8}{3}$ = 629.2 TPD-S

Flow = $87,000 + 290,000 + \frac{150,500}{3}$ = 427,000 SCFM

This implies 2.3% SO_2 conc.

This implies necessity of preheater cap. add'l.

This alternative is not recommended due to low % SO_2.

4. Roaster + Converter + 2 Reverbs

Sulfur input = $349.9 + 245.7 + \frac{2(100.8)}{3}$ = 662.8 TPD-S

Flow = $290,000 + 87,000 + 2(\frac{150,500}{3})$ = 475,000 SCFM

This implies 2.2% SO_2 concentration

This implies necessity of add'l preheater capacity

This alternative is not recommended due to low % SO_2

5. Roaster + Converter + 3 Reverbs

Sulfur input = 349.9 + 245.7 + 100.8 = 696.4

Flow = 290,000 + 87,000 + 150,500 = 530,000 SCFM

This implies 2.1% SO_2 concentration

This implies necessity of add'l preheater capacity

This alternative is not recommended due to low % SO_2

6. Route roaster and reverb offgas to a concentrator, then combine this with converter and route to acid plant

Total sulfur input = 245.7 + 100.8 + 349.9 = 696.4 TPD-S

Flow = $\frac{(349.9 + 100.8) \times 11.2}{1440} \times 2000 + 87,000$ = 94,000 SCFM

This implies an 11.5% SO_2 concentration

This implies that a D.C. acid plant may be used

Acid plant cap. needed = $696.4 \times \frac{98}{32}$ = 2133 TPD acid

Cost --

2133 TPD D.C. acid plant	= $27,000,000
Concentrator	12,000,000
	$39,000,000

7. Combine converter gas with gas from 1 operating roaster and route to acid plant

Total sulfur input = $245.7 + \frac{349.9}{18} = 265.1$

Flow = $87{,}000 + \frac{290{,}000}{18} = 103{,}000$ SCFM

This implies a 4.0% SO_2 conc.

Acid plant cap. needed = $265.1 \times \frac{98}{32}$ = 812 TPD acid

Cost --

800 TPD S.C. acid plant = $14,500,000	14,500,000
$\left(\frac{103}{80}\right)^{.6} \times 7{,}250{,}000 - 7{,}250{,}000$ = flow cap. =	1,190,000
	$15,690,000

8. Combine Converter + 1 Reverb and route to acid plant

Total sulfur input = $245.7 + \frac{100.8}{3} = 279.3$ TPD-S

Flow = $87{,}000 + \frac{150{,}500}{3} = 137{,}000$ SCFM

This implies a 3.1% SO_2 concentration

This implies a need for add'l prehtr. capac.

Acid plant cap. needed = $279.3 \times \frac{98}{32}$ = 855 TPD acid

Cost --

850 TPD S.C. acid plant	=	$15,000,000
preheater cost	=	2,250,000 (15%)
flow cap. cost = $\left(\frac{137}{70}\right)^{.6} \times 7{,}500{,}000 - 7{,}500{,}000$	=	3,740,100
		$20,990,000

Operating cost = $\frac{137}{85} \times 433{,}000 \times .60$ = $419,000/yr (Prehtr.)

9. Route Roaster gases thru a concentrator, combine with reverb, and route to an acid plant

Total sulfur input = 349.9 + 100.8 = 450.7 TPD-S

$$\text{Flow} = \frac{349.9 \times 11.2 \times 2000}{1440} + 150{,}500 = 156{,}000 \text{ SCFM}$$

This implies a 4.5% SO_2 conc.

Acid plant cap. needed = 1380 TPD acid + $450.7 \times \frac{98}{32}$

Cost --

1400 TPD S.C. acid plant	= $20,100,000
Concentrator	12,000,000
	$32,100,000

10. Route Roaster gases thru a converter, then combine concentrated stream with 1 Reverb gas, then route to acid plant

Total input sulfur = $349.9 + \frac{100.8}{3}$ = 383.5 TPD-S

$$\text{Flow} = \frac{349.9 \times 11.2 \times 2000}{1440} + \frac{150{,}500}{3} = 55{,}600 \text{ SCFM}$$

This implies a 12.6% SO_2 conc.

This implies that a D.C. acid plant may be used

Acid plant cap. needed = $383.5 \times \frac{98}{32}$ = 1174 TPD acid

Cost --

1175 D.C. acid plant	= $20,200,000
Concentrator	= 12,000,000
	$32,200,000

11. Enrich the O_2 gases then combine with gases from converters, then route to an acid plant

Total Sulfur input = 100.8 + 245.7 = 346.5 TPD-S

Flow is not determinable but will be something less than 87,000 + 156,000 = 243,000 SCFM. We will assume that the flow will not be abnormal for this size acid plant. Also we will assume that this stream will contain 4.1 - 4.3% SO_2.

Acid plant cap. needed = 1061 TPD acid

Cost --

1060 TPD S.C. acid plant	= $17,200,000
O_2 injection equipment	= 250,000
	$17,450,000

Operating costs for O_2 and fuel are subject to further development of this technique.

ALTERNATIVE CONTROL PLAN CALCULATIONS
ASARCO/HAYDEN

1. Upgrade existing acid plant to handle all converter offgases

   Input sulfur = 296 PTD-S

   Flow = 100,000 SCFM

   This implies a 4.6% SO_2 concentration

   Acid plant capacity needed = $296 \times \frac{98}{32} - 750 = 157$ TPD acid

   Cost --

   160 TPD S.C. acid plant = $5,200,000

2. Route 8 operating roaster offgases with converter offgases to upgraded existing acid plant

   Input Sulfur = 135 + 296 = 431 TPD-S

   Flow = 100,000 + 100,000 = 200,000 SCFM

   This implies a 3.35% SO_2 concentration

   This implies that added preheater cap. is needed

   Acid plant cap needed = $431 \times \frac{98}{32} - 750 = 570$ TPD acid

   Cost --

570 TPD acid plant (S.C.)	= $11,300,000
Preheater capacity	= 1,695,000 (15%)
Add'l flow cap = $\left(\frac{200}{130}\right)^{.6} \times 5,650,000 - 5,650,000$	= 1,661,100
	$14,656,100

   Operating cost = $\frac{200}{85} \times 433,000 \times .40 = \$408,000$/yr. (Prehtr.)

3. Combine offgases from 3 operating roasters with converter offgases and route to upgraded acid plant

   Total input sulfur = $296 + \frac{3}{8}(135) = 347$ TPD-S

Flow $100,000 + \frac{3}{8}(100,000) = 137,500$ SCFM

This implies a 4.0% SO_2 concentration

Acid plant capacity needed $= 347 \times \frac{98}{32} - 750 = 313$ TPD acid

Cost --

300 TPD S.C. acid plant	= $7,700,000
Add flow cap = $\left(\frac{137}{100}\right)^{.6} \times 3,850,000 - 3,850,000$	= 800,800
	$8,500,800

4. Combine offgases from 1 Reverb with converter offgases and route to upgraded acid plant.

Total input sulfur $= 296 + \frac{100}{2} = 346$ TPD-S

Flow $= 100,000 + \frac{220,000}{2} = 210,000$ SCFM

This implies a 2.6% SO_2 concentration

This implies the need for add'l preheater capacity

Acid plant cap. needed $= 346 \times \frac{98}{32} - 750 = 310$ TPD Acid

Cost --

300 TPD S.C. Acid Plant	= $7,600,000
Add'l flow cap = $\left(\frac{210}{100}\right)^{.6} \times 3,800,000 - 3,800,000$	= 2,131,800
Preheater cap	1,140,000 (15%)
	$10,871,800

Operating cost $= \frac{210}{85} \times 433,000 \times .80 = \$856,000$/yr. (Prhtr.)

5. Combine offgases from both reverbs with offgases from converters and route to upgraded acid plant.

Total sulfur input = 296 + 100 = 396 TPD-S

Flow = 100,000 + 220,000 = 320,000 SCFM

This implies 1.9% SO_2 concentration

This implies that add'l preheater cap. is required

Acid plant capacity needed = $396 \times \frac{98}{32} - 750 = 463$ TPD acid

Cost --

1213 TPD S.C. Acid plant	= $10,000,000
add'l flow cap = $\left(\frac{320}{120}\right)^{.6} \times 5{,}000{,}000 - 5{,}000{,}000$	= 4,000,000
Preheater cap.	1,500,000 (15%)
	$15,500,000

Operating cost = $\frac{320}{85} \times 433{,}000 \times 1.0$ = $1,630,000/yr (Prehtr.)

6. Route combined roaster and reverb gases to a concentrator, combine concentrated stream with converter gas, route to upgraded acid plant.

Total sulfur input = 135 + 100 + 296 = 531 TPD-S

Flow = $100{,}000 + \frac{(135 + 100) \times 11.2 \times 2000}{1440}$ = 103,700 SCFM

This implies an 8.0% SO_2 concentration

This implies that a D.C. acid plant can be used.

Acid plant cap. needed = $531 \times \frac{98}{32} - 750 = 876$ TPD acid

Cost --

876 TPD D.C. acid plant	= $17,000,000
Concentrator	12,000,000
Convert 750 TPD to DC	2,000,000
	$31,000,000

7. Route roaster gases thru a concentrator, combine with 2 reverb gases, and route to an upgraded acid plant

   Total sulfur input = 135 + 100 = 235 TPD-S

   Flow = 220,000 + $\frac{135 \times 11.2 \times 2000}{1440}$ = 222,100 SCFM

   This implies a 1.6% SO_2 concentration

   This alternative is not recommended due to low % SO_2.

8. Route roaster gases thru a concentrator, combine with gases from 1 reverb, and route to an upgraded acid plant

   Total sulfur input = 135 + 50 = 185 TPD-S

   Flow = 110,000 + $\frac{135 \times 11.2 \times 2000}{1440}$ = 112,100 SCFM

   This implies a 2.6% SO_2 concentration

   This alternative is not recommended due to low % SO_2

9. Route gases from 2 Reverbs thru a concentrator, combine with roaster gases, and route to an upgraded acid plant

   Total sulfur input = 100 + 135 = 235 TPD-S

   Flow = $\frac{100 \times 11.2 \times 2000}{1440}$ + 100,000 = 101,600 SCFM

   This implies a 3.6 % SO_2 concentration

   This alternative is not recommended due to low % SO_2

10. Enrich the reverb gases with O_2 and route to new acid plant

    Total sulfur input = 114 + 100 = 214 TPD-S

    Flow into new acid plant is less than 220,000 SCFM and concentration is - 4.0% SO_2

    Add'l acid plant capac. needed = 100 x $\frac{98}{32}$ = 306 TPD acid

Cost --

300 TPD S.C. Acid Plant	= $7,500,000
O_2 injection equipment	= 250,000
	$7,750,000

Operating costs for O_2 and fuel are subject to further development of this technique.

ALTERNATIVE CONTROL PLAN INFORMATION

MAGMA SMELTER

1. Combine all reverb offgases with converter offgases and route into present acid plant with additional capacity.

   Total sulfur input plant = 660.9 + 259 = 920 TPD-S

   Total flow into plant = 284,000 + 187,000 = 471,000 SCFM

   This implies a 3.1% SO_2 concentration

   This implies that above normal preheating capacity is required.

   Total output of plant = 2817 TPD acid

   Assuming the plant is now operating at full capacity (2065 TPD), this implies that an additional 793 TPD acid capacity must be added.

Cost --

S.C. acid plant 752 TPD	= $13,800,000	
Add'l preheater capac.	= 2,080,000	(15%)
Add'l volume flow capac.	= 5,000,000	
	$20,870,000	Total

Operating cost for preheater = $\frac{471}{85} \times 433{,}000 \times 0.6 = \$1{,}440{,}000$

2. Add a concentration unit onto reverb offgases, then combine with converter offgases and route into present acid plant with additional capacity.

   Total sulfur into plant = 920 TPD-S

   Total flow into plant = $187{,}000 + \frac{259 \times 11.2 \times 2000}{1440} = 191{,}000$ SCFM

   This implies a 7.5% SO_2 concentration

   This implies that a D.C. acid plant may be used

Also required is 793 TPD acid capacity added

Cost --

Concentration unit	= $12,000,000	
Upgrade 2100 TPD S.C. to D.C.	= 3,000,000	
Add'l D.C. acid plant cap. 252 TPD	= 15,500,000	
	$30,500,000	Total

3. Add O_2 enrichment to reverb gases then route to new acid plant

New plant input sulfur = 259 TPD-S

Total flow into plant 284,000 SCFM @ 4.0% SO_2

New plant must have 793 TPD acid

Cost --

793 TPD S.C. acid plant	= $14,300,000	
O_2 injection equipment	= 250,000	
	$14,550,000	Total

Operating costs for O_2 and fuel may be determined by further development of this technique

4. Combine offgases from 1 Reverb with Converter offgases and route to present acid plant with added capacity.

Total sulfur to plant -- 661 + $\frac{259}{3}$ = 747 TPD-S

Total flow = 187,000 + $\frac{284,000}{3}$ = 282,000 SCFM

This implies 4.1% SO_2 concentration

264 TPD additional acid plant capac. required $\left(\frac{259}{3} \times \frac{98}{32}\right)$

Cost --

264 TPD S.C. acid plant $7,000,000

5. Combine offgases from 2 Reverbs with converter offgases and route to present acid plant with added capacity.

Total sulfur to plant = $661 + \frac{2(259)}{3} = 834$ TPD-S

Total flow = $187{,}000 + \frac{2(284{,}000)}{3} = 377{,}000$ SCFM

This implies 3.4% SO_2 concentration

This implies that above normal heating capacity is required.

529 TPD Additional acid plant capacity required $\left(\frac{2(259)}{3} \times \frac{98}{32}\right)$

Cost --

529 TPD S.C. acid plant	= $10,900,000	
Additional preheater cap.	1,635,000	(15%)
Additional volume flow cap. $\left(\frac{377}{270}\right)^{.6} \times 12{,}500{,}000 - 12{,}500{,}000$ =	2,787,500	
	$15,322,500	Total

Operating cost -

$\frac{377}{85} \times 433{,}000 \times .4$ = $768,000/Yr. (prehtr.)

6. Route all reverb gases into new acid plant

Total sulfur into plant = 259 TPD-S

Total flow into plant = 284,000 SCFM

This implies 1.5% SO_2 concentration

This implies necessity of continuous preheating and refrigeration

Total output of plant = 793 TPD acid

Cost --

S.C. acid plant 800 TPD	=	$14,400,000
Additional preheater/refrig. cost	=	4,320,000 (30%)
Additional volume flow cap.	=	9,432,000
		$28.152,000 Total

Operating cost --

$$\frac{284}{85} \times 433{,}000 \times 1.0 = \$1{,}447{,}000 \text{ (preheater)}$$

$$\frac{800}{900} \times 340 \times 24 \times 18 = 130{,}500 \text{ (refrig.)}$$

$$\$1{,}577{,}500$$